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1903. Vol. LXXXIV. Part II.

LONDON :

GURNEY & JACKSON, 10, PATERNOSTER ROW

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JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Optical Rotation of Organic Compounds. L. A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 606—622. Compare Abstr., 1898, ii, 274 and 495; 1899, ii, 3).—The author brings forward further evidence in support of the two principles previously (*loc. cit.*) enunciated by him, namely: (1) The approximation to a constant value of the molecular rotation in a homologous series as the series is ascended, and (2) the moderating effect observed when a substituent group enters an optically active molecule at a distance from the active complex. The first of these principles is exemplified by the molecular rotations of the menthyl esters of the fatty acids, which are as follows:

Menthol	- 78.0	Menthyl <i>n</i> -valerate ...	- 157.3
Menthyl formate	- 146.3	„ <i>n</i> -hexoate.....	- 157.7
„ acetate.....	- 157.3	„ <i>n</i> -heptoate ...	- 157.7
„ propionate ...	- 160.2	„ <i>n</i> -octoate	- 155.8
„ <i>n</i> -butyrate ...	- 156.9	„ <i>n</i> -nonoate ...	- 157.3

A number of other menthyl derivatives, some of them not previously

prepared, have been examined, the results being given in the following table:

	Sp. gr. at 20°/4°.	$[\alpha]_D$.	$[M]_D$.
Menthyl <i>n</i> -nonylate.....	—	—	- 157·3°
„ methyl ether.....	0·8607	- 95·67°	- 162·6
„ ethyl ether	0·8357	- 97·29	- 179·0
„ propyl ether.....	0·8519	- 92·14	- 182·5
„ benzyl ether.....	0·95131	- 94·62	- 232·7
<i>l</i> -Menthylamino	0·8562	- 36·15	- 56·03
Menthyl dimethylamine	0·8465	- 58·66	- 107·35
Menthyl diethylamine	0·8487	- 114·80	- 242·20
Menthyl dipropylamine	0·8490	- 130·75	- 312·50
Menthyl dibutylamine.....	0·8494	- 114·35	- 305·30
Menthyl ethylamine.....	0·8448	- 83·45	- 152·71
Menthyl chloroacetate	1·0564	- 73·86	- 171·2
„ dichloroacetate.....	1·1088	- 63·56	- 168·7
„ trichloroacetate	1·1796	- 59·05	- 176·8
„ bromoacetate	1·2136	- 60·95	- 168·8
„ α -bromopropionate	1·1762	- 54·52	- 158·6
„ isobutyrate	0·9062	- 69·76	- 157·7
„ cyanoacetate (in benzene)	—	- 80·71	- 180·0
„ benzoate („).....	—	- 90·92	- 236·3
„ <i>o</i> -bromobenzoate	1·2287	- 60·55	- 205·3
„ <i>m</i> -bromobenzoate.....	1·2342	- 70·43	- 238·7
„ <i>p</i> -bromobenzoate	1·2264	- 70·45	- 238·8
„ phenylpropionate.....	0·9851	- 56·21	- 161·9
„ cinnamate	1·0066	- 86·65	- 247·8
„ <i>p</i> -nitrobenzoate (in benzene)	—	- 88·37	- 269·5
„ β -naphthoate („).....	—	- 92·76	- 287·6
„ crotonate	0·8325	- 82·61	- 185·0
„ oxalate (in benzene) ...	—	- 101·5	- 371·5
„ succinate („) ...	—	- 81·52	- 321·2
„ suberate („) ...	—	- 73·30	- 330·1
„ orthosilicate („) ...	—	- 95·24	- 617·1

The points to be noticed in the above table are: (1) The great increase in the molecular rotation caused by the introduction of a benzene nucleus into the active molecule. (2) The great difference between the values for the isomerides, dimethyl- and ethyl-menthylamine. (3) The small change produced by the substitution in menthyl acetate of chlorine atoms, these being at some distance from the active complex. (4) The values for the menthyl esters of di- and tetra-basic acids these being respectively about twice and four times the values for the esters of the fatty acids.

The author discusses the papers of Guye and Babel (Abstr., 1899, ii, 718 and 719), whose results he considers confirmatory of his own views.

T. H. P.

Stereochemistry of Alicyclic Compounds. OSSIAN ASCHIAN (*Ber.*, 1902, 35, 3389—3399).—The author draws attention to the limitations of the van't Hoff and Le Bel hypotheses when applied to

alicyclic compounds. It is shown in detail that the possibilities of isomerism in ring systems are more truly seen when the symmetry of the molecule is alone considered; further, it is demonstrated on these lines that optical activity becomes possible in certain ring systems in the absence of an asymmetric carbon atom.

This interesting paper cannot be suitably abstracted in detail.

K. J. P. O.

Optical Double-Isomerism. GÖSTA HARTWALL (*Ber.*, 1902, 35, 3399—3400).—On heating together mol. proportions of citraconic anhydride and *l*-borneol at 100° under pressure, a mixture of two acid esters is obtained, both of which, on hydrolysis, yield borneol and the acid unchanged. One acid ester forms large crystals melting at 150.5° and has $[\alpha]_D - 39.97^\circ$ at 17.5°, and $- 39.93^\circ$ at 18° in alcoholic solution; the other acid ester forms four-sided leaves or prismatic crystals melting at 82.5°, and has $[\alpha]_D - 43.44^\circ$ at 22° and $- 43.27^\circ$ at 20.5°. The optical antipodes of these two acids were prepared from the anhydride and *d*-borneol. An acid ester was prepared from mesaconic acid and *l*-borneol by heating the two substances together under pressure at 135°; it crystallised in aggregates of prismatic crystals melting at 116.5° and has $[\alpha]_D - 45.14^\circ$ at 21° and $- 45.13^\circ$ at 20° in alcoholic solution.

K. J. P. O.

Limit of the Intensity of a Current from a Voltaic Element capable of producing Appreciable Electrolysis in a Voltameter. MARCELIN P. E. BERTHELOT (*Compt. rend.*, 1902, 135, 485—492. Compare Abstr., 1902, ii, 546, 547, 591).—In a voltameter containing only dilute sulphuric acid, the external pressure exerts such an influence that as it diminishes a greater resistance may be introduced into the circuit, and there will still be appreciable electrolysis. The concentration of the acid scarcely modifies the intensity of the current required to produce appreciable electrolysis, but in this respect the influence of temperature is very great.

With pyrogallol in the voltameter, the effect of the external pressure is the same as without it, and the concentration of the acid has no influence, but when a large excess of pyrogallol is used the cohesion of the liquid is so modified that the bubbles of hydrogen are evolved less freely.

From the results of his various observations, the author concludes that when a feeble current passes through a liquid the chemical energy necessary to start the action is always present, but not sufficient to maintain it, and external electrolysis can only be effected if it is maintained by a current which is continuous and above a certain limit.

The evolution of hydrogen in a voltameter is incomparably more sensitive than the deposition of silver.

The order of magnitude of the reactions taking place in the voltaic elements studied by the author is comparable with those of normal physiological phenomena, and the formation of hydrochloric acid in the gastric juice can be explained as due to the cumulative action of the various cells of the body.

J. McC.

Electrical Conductivity and Viscosity of Casein Solutions. OTTO SACKUR (*Zeit. physikal. Chem.*, 1902, 41, 672—680).—A solution containing 1 gram of dried casein requires for neutralisation (with phenolphthalein as indicator) 8.81 c.c. of $N/10$ sodium, barium, or calcium hydroxide. Hence the equivalent of casein is 1135, and its molecular weight must be a multiple of this number. The conductivity of solutions of the casein sodium salt varies with the dilution in a manner which points to the basicity of casein being 4, and possibly 5 or 6. Although this casein sodium salt is an electrolyte, it does not diffuse through parchment.

The values obtained for the viscosity of casein sodium salt solutions are in accordance with Arrhenius's formula $\eta = A^n$ (Abstr., 1888, 336); it is shown that the viscosity of the solutions is mainly due, not to the free casein produced by hydrolysis and dissolved in colloidal form, but to the casein-sodium molecule or its ion (compare Reyher, *Zeit. physikal. Chem.*, 1888, 2, 743).

When casein dried at 100° is treated with dilute alkalis, a substance similar to casein has been obtained, and has been called *isocasein*. The behaviour of this substance, which is more strongly acid than casein, has been studied on the lines mentioned above. J. C. P.

Temperature Coefficients of Electrical Conductivity of Solutions in Water and in Organic Solvents. Influence of Superfusion and of Maximum Density. GIACOMO CARRARA and M. G. LEVI (*Gazzetta*, 1902, 32, ii, 36—53).—After giving a short account of previous investigations made on the relations existing between the physical properties of solvents and their dissociating power, the authors describe their own experiments, which consist of a number of measurements of electrical conductivity by Kohlrausch's method, using an alternating current and a telephone; special precautions were taken to keep the temperature constant to within 0.1° for 15 minutes. For the carefully purified solvents employed, the following results were obtained:

	Boiling point.	Specific gravity.	Specific conductivity.
Methyl alcohol.....	64.5° (759 mm.)	0.79375 at $25^\circ/4^\circ$	$2.5.10^{-6}$ at 25°
Ethyl „	78 (758 mm.)	0.79425 at $16^\circ/4^\circ$	$1.3.10^{-6}$ at 25°
Acetone	57.5° (761 mm.)	0.79729 at $20^\circ/4^\circ$	$0.6.10^{-6}$ at 25°
Pyridine	114.5° (763 mm.)	0.99937 at $0^\circ/4^\circ$	$0.96.10^{-6}$ at 25°
Formic acid (melting at 7.4°)	101 (760 mm.)	1.24405 at $0^\circ/4^\circ$	$0.1705.10^{-4}$ at 17°

The conductivity results obtained by the authors for solutions of the same, or nearly the same, concentrations of potassium iodide in various solvents are given in the following table, which contains also various other physical constants of the different solvents obtained by Walden and Centnerszwer (Abstr., 1902, ii, 245); V represents the dilution in litres of solution containing a gram-molecule of the potassium iodide, K the observed conductivity in reciprocal ohm units, and C_t its temperature coefficient, relative either to 0° or 18° , calculated from the formula:

$$C_t = (K_1 - K_2)/K_0(t_1 - t_2) \text{ or } C_t = (K_1 - K_2)/K_{18}(t_1 - t_2).$$

Solvent.	V .	K_0 .	$C_t(0)$.	$C_t(18^\circ)$.	Dielectric constant.	Factor of association.	Latent heat of evaporation.	Viscosity.	Surface tension.
Water	195.7	0.002267	0.0320	0.0208	81.12	3.7	536.2	0.0089	33.6
Formic acid.....	200	0.001800	0.0245	0.0173	57.0	3.6	103.7	0.0162	64.3
Formic acid (for KCl)	100	0.002510	0.0270	0.0180	57.0	3.6	103.7	0.0162	64.3
Methyl alcohol...	197.6	0.001468	0.0168	0.0129	32.5	3.4	267.0	0.0055	59.8
Ethyl alcohol...	200	0.000845	0.0225	0.0164	26.8	2.7	205.1	0.0110	38.5
Acetone	160	0.005173	0.0090	0.0079	20.7	1.09	125.3	0.0020	33.6
Pyridine	200	0.00090	0.0170	0.0094	20.0	0.93	101.4	—	31.1

It will be seen from these numbers that, in general, a certain parallelism exists between the temperature coefficients of the conductivity and the physical constants given, the principal exception to such parallelism being found in the viscosity.

Temperature conductivity curves, in some cases for various dilutions, are given for potassium chloride and iodide, cadmium iodide, sodium nitrate, and acetic and monochloroacetic acids in water; potassium chloride in formic acid; potassium iodide in formic acid, in methyl and ethyl alcohols, and in acetone and pyridine. The curves for aqueous solutions exhibit a marked difference from those in organic solvents. The latter can be represented as relations of the first degree, whilst the curves for aqueous solutions cannot be expressed even as a second degree relation, owing to the anomalies which are introduced in the neighbourhood of the temperature of maximum density of water and which are most clearly shown in solutions of feeble electrolytes. These results are in agreement with the observations of Lussana (*Atti Reg. Ist. Venet.*, 1893, [vii], 4) and Gnesotto (*ibid.*, 1900, 59, ii, 987). These anomalies are due to a variation in the ionic concentration, but it seems that this does not depend only on the diminution in volume of the solvent and on the special condition (subjected, that is, to something resembling a pressure) in which the electrolyte is found, since this would not explain why the effect is most marked with weak electrolytes. The authors' view is that the phenomenon depends, in great part, on the non-homogeneity of water at its maximum density, crystalline molecular aggregates being formed which do not participate in the equilibrium determining the limit of the degree of dissociation between solvent and solute. T. H. P.

Behaviour of a Lead Anode in Solutions of Sodium Hydroxide and the Electrolysis of Solutions of Sodium Hydroxide containing Lead. KARL ELBS and J. FORSELL (*Zeit. Elektrochem.*, 1902, 8, 760—772).—When a clean lead anode is used in a solution of sodium hydroxide (the current density being small), the metal passes into solution as bivalent lead. When the solution has become saturated with lead oxide, or if a solution of lead oxide in sodium hydroxide is employed, lead peroxide is deposited on the anode with small current densities, but as the current increases lead oxide and

oxygen are also formed, the yield of lead peroxide diminishing; at higher temperatures, it increases rapidly. These observations are best explained by supposing that HPbO_2 ions are discharged at the anode; these decompose into water, lead oxide, and oxygen, which react more or less completely to form lead peroxide.

This interpretation is also in agreement with measurements of the discharge potentials. It is found that lead peroxide is formed on a platinum anode at 20° at a potential 0.23 volt lower than that required for the formation of lead oxide and oxygen. Lead peroxide appears to occlude oxygen in the same way as platinum. The potential difference between a lead peroxide coated platinum electrode and a solution of lead oxide in sodium hydroxide is about 0.3 volt below that required for the formation of PbO_2 ; hence the deposition and solution of PbO_2 electrolytically are not reversible operations.

T. E.

Electrolysis of Mixtures of Salts. ANATOLE LEDUC (*Compt. rend.*, 1902, 135, 395—396).—In order to investigate the effects of impurities on observations based on the use of a silver nitrate voltameter, two such voltameters were employed, one containing pure silver nitrate, the other silver nitrate to which potassium nitrate or copper nitrate had been added. It was found that, unless the concentration of the impurity was very excessive, no difference in the quantity of metal deposited was observed. Admixture with the salt of a metal higher in the potential list than silver would probably cause other results, but such impurity would soon be eliminated during electrolysis.

L. M. J.

Nature of Cadmium Amalgams and their Electromotive Behaviour. H. C. BIJL (*Zeit. physikal. Chem.*, 1902, 41, 641—671).—The complete freezing point curve for mixtures of cadmium and mercury has been determined, and is found to rise regularly from the freezing point of mercury to that of cadmium, there being only a slight discontinuity at 188° and 65 atomic per cent. of cadmium. The temperature at which separation of solid begins has been determined also for many of the amalgams by studying the volume change which accompanies rise of temperature. The expansion during the process of fusion is greater than that for either the solid or liquid amalgam, so that both the beginning and the end of fusion can be determined. In this way, it has been shown that from amalgams containing 0—65 atomic per cent. of cadmium, mixed crystals separate containing 0—75 atomic per cent. of cadmium, whilst from amalgams containing 65—100 atomic per cent. of cadmium mixed crystals separate containing 77—100 atomic per cent. of cadmium; there is therefore a gap in the mixed crystal series from 75 to 77 per cent. The lower the temperature the wider is this gap; thus at 25° it extends from 65 to 80 atomic per cent., which means that an amalgam containing a percentage of cadmium between these two limits will at 25° separate into two phases. This extension of the gap at lower temperatures has been demonstrated by studying at a definite temperature the *E.M.F.* of cells of the following type:— $\text{Hg} \mid \text{Hg}_2\text{SO}_4, \text{CdSO}_4 \mid \text{Cd}$ amalgam. The *E.M.F.* of such a cell

gradually increases with the percentage of cadmium in the amalgam, but remains constant for intervals where the cadmium amalgam consists of two phases (compare Wind, Abstr., 1901, ii, 368). If *E.M.F.* is plotted against Cd concentration, and the curves for 25°, 50°, and 75° are compared, the horizontal parts, corresponding with the gap in the mixed crystal series, increase in length as the temperature of investigation is lowered. In the light of the results obtained, the irregularities of the Weston cadmium cell observed by Jaeger and Cohen (see *loc. cit.*) may be explained.

The author has also determined the heat developed when 1 gram-atom of cadmium is dissolved in amalgams of different concentration.

J. C. P.

Electrolytic Reduction of Potassium Chlorate. G. H. BURROWS (*J. Physical Chem.*, 1902, 6, 417—426).—When potassium chlorate solution is electrolysed with copper electrodes, a high reduction efficiency which may reach 200 per cent. is obtained. This does not appear to be due to spontaneous decomposition, as no evolution of oxygen is observed, neither is perchlorate formed. The efficiency is increased by high current density at the anode and is decreased by the presence of free alkali. Possible causes for the high efficiency are considered, one of these being reduction by the metal itself at the cathode.

L. M. J.

Latent Heat of Vaporisation of Aniline, *o*-Toluidine, certain of their Derivatives, and other Organic Substances. WLADIMIR LUGININ (*Ann. Chim. Phys.*, 1902, [vii], 27, 105—144. Compare Abstr., 1901, ii, 145; 1902, ii, 547).—The following values are published for the first time:

	Latent heat of vaporisation.	Specific heat.	
<i>o</i> -Toluidine	95·085	0·5239	between 195° and 22°
Methylaniline	95·07	0·5126	„ 196 „ 20
Dimethylaniline	80·69	0·4822	„ 188 „ 20
Dimethyl- <i>o</i> -toluidine ...	70·25	0·4949	„ 185 „ 20
Dichloroacetic acid	79·10	0·3498	„ 196 „ 21
Propionic acid	91·44	0·5596	„ 138 „ 20
Nitrobenzene	79·15	0·3963	„ 200 „ 20

On applying Trouton's rule to these results, it is found that the four aromatic bases and nitrobenzene are not polymerised in the liquid state; the two aliphatic acids, however, exhibit considerable polymerisation.

	Variation in the b. p. per 1 mm. press.		B. p. at 760 mm.
Aniline.....	0·053	between 700 mm. and 760 mm.	184·25
<i>o</i> -Toluidine ...	0·054	„ 720 „ 760	„ 198·12
Methylaniline	0·052	„ 720 „ 760	„ 191·36

	Variation in the b. p. per 1 mm. press.					B. p. at 760 mm.
Dimethylaniline	0.056	between	720 mm.	and	760 mm.	192.68
Dimethyl- <i>o</i> -toluidine..	0.056	"	700	"	760 "	183.90
Dichloroacetic acid ...	0.049	"	700	"	760 "	194.42
Propionic acid.....	0.043	"	720	"	760 "	140.30
Methylethylacetoxime	0.044	"	700	"	760 "	181.89
Anisole.....	0.051	"	700	"	760 "	153.53
Butyronitrile	0.049	"	700	"	760 "	117.40
Nitrobenzene	0.059	"	700	"	760 "	210.60

G. T. M.

Volatility of Carbon Compounds in Relation to Molecular Weight and Formula. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1902, 537—582).—From a study of the boiling points of a number of different groups of organic compounds, and the change in the boiling point accompanying certain changes in the constitution and molecular weight of substances, the author shows how these differences may be employed as a guide in the assignment of the formula to a substance. The change in the boiling point due to certain changes in the constitution of the compound is determined, and where marked deviations from the normal behaviour are met with, they are taken as a sign of a difference in the constitution or molecular weight from that assigned to the particular substance. In this way, abnormally high boiling points were found in the case of butyrolactone, succinic anhydride, ethylene carbonate, succinate, fumarate, glycollate, and oxalate, glycollide, dialkyl esters of oxalic acid, and aminoacetic acid. In several cases, these indications of a higher molecular complexity were confirmed by cryoscopic determinations.

A. F.

Freezing Point of Dilute Solutions of Mixtures. YŪKICHI OSAKA (*Zeit. physikal. Chem.*, 1902, 41, 560—564).—Determinations were made of the freezing point of solutions of potassium sulphate and mannitol, potassium sulphate and phenol, sodium chloride and carbamide, and sodium chloride and phenol. It was found that in general the cryoscopic depression of the mixture is but slightly different from the sum of the depressions of the components; it is usually slightly smaller. The author considers that the influence of the ions of the salt on the undissociated compound is very small and that such an influence cannot therefore be the principal cause of the departure of strong electrolytes from the mass-action law.

L. M. J.

A Thermochemical Constant. FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1902, 24, 882—892).—The heats of formation of organic substances, determined by Thomsen, are those obtained by combustion to gaseous carbon dioxide and liquid water. The molecular heat of formation of gaseous water at 18° is about 57934 cals., but for liquid

water the value used by Thomsen is 68357 cals., and if the difference, 10423 cals., be subtracted as many times as there are molecules of water produced, from the heat of combustion of any organic substance as given by Thomsen, a series of values is obtained in which the author has noticed a particular regularity.

If the number of molecules of carbon dioxide produced be represented by a , the number of water molecules produced by b , the number of oxygen molecules dissociated by c , and by n the number of atomic linkings in the substance burned, then $4K/(12a + 6b - c - 8n) = \text{constant}$, where K is the heat of combustion of a hydrocarbon. The value of the constant is about 13880. The value of n is independent of the nature of the linkings, and is equal to the number of atoms in the molecule *minus* one. For cyclic compounds, a constant factor must be introduced to represent the strength of the ring.

For organic substances containing chlorine, the constant is found from $4K/(12a + 6b + h - c - 8n)$, where h is the number of chlorine molecules produced; the formula for bromides is the same with $2h$ in place of h , and for iodides h is replaced by $4h$. For compounds containing nitrogen, the divisor, in the case of cyanogen derivatives, is $12a + 6b + 3m - c - 8n$, m being the number of nitrogen molecules set free; for amines, it is $12a + 6b + 9m - c - 8n$. The divisor becomes $12a + 6b + 9s - c - 8n$ in the case of sulphur compounds, s being the number of molecules of sulphur dioxide produced. The constant in the case of alcohols is found from $4K/(12a + 6b - c - c_1 - 8n)$, where c_1 is the number of oxygen molecules contained in the alcohol.

The average value obtained for 66 compounds belonging to the different series is 13773.

The author deals with the significance of this constant and shows that it suggests a general law. In any class of compounds, the heat of formation is proportional to the number of atomic linkings within the molecule, and seems to bear no relation to the masses of the atoms which are combined.

J. McC.

Measurement of Temperature. Part I. Pressure Coefficients of Hydrogen and Helium at Constant Volume and at Different Initial Pressures. Part II. Vapour Pressures of Liquid Oxygen at Temperatures below its Boiling Point on the Constant Volume Hydrogen and Helium Scales. Part III. Vapour Pressures of Liquid Hydrogen at Temperatures below its Boiling Point on the Constant Volume Hydrogen and Helium Scales. MORRIS W. TRAVERS, GEORGE SENTER, and ADRIEN JAQUEROD (*Proc. Roy. Soc.*, 1902, 70, 484—491).—Between 0° and 100°, the coefficient of increase of pressure at constant volume is 0.00366255 for both hydrogen and helium; further, this number is independent of the initial pressure, although the values obtained for the coefficient at lower initial pressures are not quite so concordant as those at higher initial pressures.

The temperatures at which the vapour pressure of liquid oxygen has values from 200—800 mm. have been determined (1) by a constant volume hydrogen thermometer, (2) by a constant volume helium thermometer; the values given by the latter are 0.1° higher than

those given by the hydrogen thermometer. The following table shows the character of the results obtained :

Vap. press. in mm.	Temp. on helium scale.	Vap. press. in mm.	Temp. on helium scale.
800.....	90.70°	500.....	86.39°
760.....	90.20	400.....	84.49
700.....	89.43	300.....	82.19
600	88.01	200.....	79.17

The temperatures corresponding with vapour pressures of liquid hydrogen from 50—800 mm., have been determined in the same two ways ; in this case, the values given by the helium thermometer are 0.2° higher than those obtained with the hydrogen thermometer. The following table summarises the results :

Vap. press. in mm.	Temp. on helium scale.	Vap. press. in mm.	Temp. on helium scale.
800.....	20.60°	400.....	18.35°
760.....	20.41	300.....	17.57
700.....	20.12	200.....	16.58
600.....	19.61	100.....	15.13
500.....	19.03	50.....	14.11

The melting point of hydrogen has been found to be 14.1° on the helium scale. Helium, when lowered in temperature to about 13° abs. and subjected to a pressure of 60 atmospheres, showed no sign of liquefaction. Solid neon, at the temperatures 20.4° and 15.65° (helium scale), has the vapour pressures 12.8 mm. and 2.4 mm. respectively. That neon is a homogeneous substance is shown by the fact that its vapour pressure does not change after successive portions have evaporated.

The pure hydrogen used in this investigation was prepared by means of spongy platinum, and the helium was obtained from cleveite gas.

J. C. P.

Physical Constants, Critical Solution Temperature, and Osmotic Pressure. LÉON CRISMER (*Chem. Centr.*, 1902, ii, 3; from *Bull. assoc. belge des Chimistes*, 16, 83—94).—The presence of 0.5—1.0 per cent. of water in alcohol cannot be satisfactorily detected either from the density or from the boiling point. On the other hand, the purity of absolute alcohol is easily proved by a determination of the critical temperature of solution in light petroleum. J. C. P.

Law of the Rectilinear Diameter. ALEXIUS BATSCINSKI (*Zeit. physikal. Chem.*, 1902, 41, 741—743).—Starting from van der Waals' equations and Dupré's formula for the vapour tension, the author arrives at the equation $v_k/V + v_k/v = 3 - 3T/n$, where v_k is the critical volume, V and v the specific volumes of gas and liquid respectively; n is proportional to the critical temperature of the substance, so that the above equation differs from the mathematical expression of Cailletet and Mathias' law only in the value of the

coefficients; this difference is probably due to the inadequacy of van der Waals' equation of condition.

The law of the rectilinear diameter has usually been described as empirical, but the author's investigation shows it to have a theoretical basis.

J. C. P.

Estimation of Very Small Vapour Tensions in Certain Circumstances. LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1902, 24, 864—865).—The vapour tension of iodine in an aqueous potassium iodide solution can be determined by passing a current of air through a weighed quantity of the solution in a thermostat. The loss of weight gives the amount of water and iodine volatilised, and by titration of the solution before and after, the loss of iodine can be determined. The vapour tension of the iodine is found from $s = wMS/mW$, where M , S , and W are the molecular weight, the vapour tension, and the weight of water respectively, and w and m are the weight and molecular weight of iodine.

J. McC.

True Density of Chemical Compounds and its Relation to Composition and Constitution. VI. Halogenated Compounds.

VII. Sulphur Compounds. INNOCENTIUS I. KANONNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 575—605. Compare Abstr., 1900, ii, 134; 1901, ii, 365; and 1902, ii, 244).—From the determination of the true densities of 80 compounds containing chlorine, the author draws the following conclusions: (1) Free chlorine possesses the molecular density, 219.0, and it has this value in many of its compounds containing more than one chlorine atom. (2) In general, however chlorine assumes a smaller molecular density when it enters into combination with other elements, the magnitude depending on the conditions under which it is found in the compound. Thus as a substituent in gaseous hydrocarbons, chlorine has the molecular density 157.5; in monosubstituted non-oxygenated compounds, 169.1; in compounds containing more than one chlorine atom, 192.3, 203.9, or 219.0, according to the amount of the halogen present. In oxygenated compounds, the value is 192.3 when one atom of chlorine is present, and 203.9 or 219.0 when there are several. (3) When two carbon atoms united by a double linking are present in a compound, a chlorine atom combining with one of these atoms breaks the double linking and forms the complex $\cdot\text{CCl}\cdot\text{C}\cdot$, in which the trivalent chlorine has the molecular density, 169.1. If, however, the chlorine atom is separated from the doubly-linked carbon atom even by one carbon atom, as, for example, in allyl chloride, such breaking up of the double linking is not effected. In order to bring the experimental values for the molecular density into accord with the calculated ones, special formulæ have been devised for certain compounds, for instance, chloroform, $\text{CCl}_2\cdot\text{CH}$, and amyl chloromaleate, $\text{CO} \begin{array}{c} \text{O}(\text{C}_5\text{H}_{11}) \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{CCl}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11}$.

Thirty-two sulphur compounds have been examined, the results leading to the conclusions: (1) Free sulphur has the molecular density 121.2, and this is also the value in those of its compounds in which it acts as a bivalent element. When the valency increases, the

molecular density increases by multiples of 23.2, so that in the quadrivalent condition, the value is 144.4, and in the sexavalent state, 167.6. (2) In compounds of different types, the molecular density of sulphur shows a behaviour resembling that of oxygen in analogous compounds; thus the value for oxygen or sulphur existing in the form $C \cdot O \cdot C$ or $C \cdot S \cdot C$ is 7.74 less than the value for the free element, whilst in $C:S$ or $C:O$, the value is increased by 4.84. T. H. P.

Dependence of Viscosity of Liquid Substances on the Temperature and Chemical Constitution. ALEXIUS BATSCHINSKI (*Chem. Centr.*, 1902, ii, 180—181; from *Bull. Soc. Imp. Nat. Moscow*, 1902, 1—23).—A large number of liquids have been examined with reference to the parameter law. Within certain limits of temperature, a constant value has been obtained for the expression $\eta(t + 273)^3$ for about half of the substances examined. Water, acids, and alcohols do not even approximately follow the law; those substances which are subject to the law below the critical temperature, as a rule follow it also above this point. At very low temperatures, the law loses its applicability. The anomalous behaviour of compounds containing a hydroxyl group is attributed to the change of association of the molecules with varying temperature.

For those substances which do not obey the law, the deviation is always in the same direction; η (the viscosity coefficient) increases more quickly with diminishing temperature than proportional to the third power of the absolute temperature. The only exception to this is carbon disulphide.

It has been deduced that for all those substances which obey the laws of corresponding conditions and viscosity parameter, the expression $M^{\frac{1}{3}}\theta^{\frac{2}{3}}Em^{\frac{2}{3}}$ has the same value (about 38.5), where M is the molecular weight, θ the critical temperature, E the viscosity-parameter, and m the true volume of the molecules. The results obtained confirm this conclusion and the formula may be used to find the critical temperature.

J. McC.

Dissociation of Mercury Haloid Salts. HARRY MORSE (*Zeit. physikal. Chem.*, 1902, 41, 769—734).—The solubility of silver chloride in mercuric nitrate solutions of different concentrations, and the distribution ratios for mercuric chloride between (1) water and toluene, (2) mercuric nitrate solutions and toluene, have been determined. It appears probable that in the solutions examined the cation $HgCl^+$ is present,—a conclusion which is confirmed by electrolytic transport experiments. With the help of the above-mentioned solubility and distribution determinations, the following equilibrium constants have been calculated: $[Hg^{++}][Cl^-]/[HgCl^+] = 0.35 \times 10^{-7}$; $[HgCl^+][Cl^-]/[HgCl_2] = 2.8 \times 10^{-7}$; $[Hg^{++}][Cl^-]^2/[HgCl_2] = 1.0 \times 10^{-14}$ (compare Luther, *Abstr.*, 1901, ii, 301); $[Hg^{++}][HgCl_2]/[HgCl^+]^2 = 0.13$. Constants have been obtained also for the parallel bromide and iodide equilibria, but in these cases the phenomena are complicated by the extensive formation of complex molecules in solution. Two such compound substances have been isolated, namely, $HgBr_2$, $Hg(NO_3)_2$ and $2AgBr$, $Hg(NO_3)_2$.

The law of mass action is found to be valid within the range of the author's experiments. Incidentally, it has been found that a solution of mercuric chloride saturated at 25° contains 71.17 grams of the salt per litre.

J. C. P.

Capillarity of Solutions. JOH. MATHIEU (*Ann. Physik.*, 1902, [iv], 9, 340—366).—When a dried pig's bladder is placed in a salt solution, the concentration of the solution absorbed is less than that of the original. The introduction of suitable electrodes allows the system to be regarded as a concentration cell, and the *E.M.F.* of this cell is a measure of the difference between the concentration of the solution and that of the portion absorbed by the bladder. Qualitatively, porous cells and tiles, parchment paper, and capillary tubes exhibit the same phenomenon. In the last case, it is found that the smaller the radius of the tube the greater is the difference of concentration produced. Hence it is not permissible to determine the surface tension of electrolytic solutions by measuring the height to which they will rise in a capillary tube.

J. C. P.

Surface Tension and Double Layer at the Common Surface of Two Solvents. F. VON LERCH (*Ann. Physik.*, 1902, [iv], 9, 434—441).—The surface tension at the common surface of water and benzene is affected by the presence of an electrolyte, and this influence is at least partly electrical in character. When the electrolyte is a neutral salt, such as sodium chloride or acetate, the surface tension is not greatly affected, but the addition of a trace either of acid or alkali to this solution produces a marked alteration in the surface tension.

A capillary electrometer can be constructed with water and benzene as the two liquids, and the observed movements of the common surface in the capillary tube can be predicted.

J. C. P.

A Consequence of the Kinetic Theory of Diffusion. J. THOVERT (*Compt. rend.*, 1902, 135, 579—580).—It is shown that for a number of non-electrolytes in aqueous solution the product MD^2 is constant, where M is the molecular weight and D the diffusion constant. The value of the constant is about 60×10^{-10} ; the molecular weight can thus be ascertained from the diffusion constant.

J. McC.

Velocity of Reaction before Complete Equilibrium and the Point of Transition are reached, &c. III. MEYER WILDERMAN (*Phil. Mag.*, 1902, [vi], 4, 468—489. *Comparo Abstr.*, 1901, ii, 544).—The paper is mainly theoretical and unsuitable for abstraction. Among the conclusions arrived at are the following:—Chemical action between substances is restricted to homogeneous systems and the regulating principle is the law of mass action. In such a case, two reactions take place simultaneously in opposite directions, and the equilibrium finally established is of a dynamic nature. On the other hand, the mutual action between different parts of a heterogeneous system is restricted to the transportation of the substance from one part of the system to another, the two regulating factors being the surface of contact of the reacting parts of the

system, and the remoteness from the point of equilibrium. The transportation takes place, therefore, according to the equation $dt/dT = K'(t_0 - t)(t - t_{0v} + K)$ (compare *loc. cit.*), and the equilibrium finally established is of a static nature. J. C. P.

Rate of the Reaction between Arsenious Acid and Iodine in Acid Solution; Rate of the Reverse Reaction and the Equilibrium between them. J. R. ROEBUCK (*J. Physical Chem.*, 1902, 6, 365—398).—The equation representing the reaction between iodine and arsenious acid may be written $\text{AsO}'''_3 + \text{I}'_3 + \text{H}_2\text{O} \rightleftharpoons \text{AsO}'''_4 + 3\text{I}' + 2\text{H}'$, and the equilibrium constant should be given by the expression ab/xy^3z^2 , where a is the concentration of the AsO'''_3 , b that of the I'_3 , x that of the AsO'''_4 , y that of the I' , and z that of the H' . The experiments completely verified this expression; the velocity of the direct reaction was found to be directly proportional to the first power of the concentration of both the arsenious acid and of the tri-iodine ion. It was also found that the velocity was approximately inversely proportional to the square of the concentration of the iodine ions and inversely proportional to the concentration of the acid if this concentration is not too high. The velocity of the reverse reaction was also investigated and found to be proportional to the first power of the concentrations of the arsenic acid, iodine ion, and acid ion, if the concentration is sufficiently low; but at higher concentration it is proportional to higher powers of the iodine and acid concentrations. The direct velocity is hence $dx/dt = kab/xy^2z$, the reverse velocity $-dx/dt = k'x.y.z$, and the equilibrium constant is $K = ab/xy^3z$, if the solutions are sufficiently dilute. L. M. J.

Reaction between Potassium Persulphate, Hydrogen Iodide, and Phosphorous Acid. WILHELM FEDERLIN (*Zeit. physikal. Chem.*, 1902, 41, 565—600).—In a mixture of phosphorous acid, hydrogen iodide, and potassium persulphate, the following reactions take place: (1) the iodine ions are oxidised to iodine by the persulphate, (2) the iodine is reduced by the phosphorous acid to iodine ions; the iodine ions hence act as a catalysor. The author's experiments were conducted in order to determine whether the total velocity of the reaction agreed with that calculated from the separate velocities. The reaction between the persulphate and iodide was found to be of the second order, as was previously shown by Price (*Abstr.*, 1899, ii, 147); the reaction between phosphorous acid and iodine was also found to be of the second order, but the observations on these reaction velocities are not recorded. The reaction between the persulphate and the phosphorous acid was found to be too slow to affect the results. Formulæ are deduced for the concentration of iodine and persulphate in the combined reaction, based on the velocity equations for the two component reactions. The results are not in good accord quantitatively with the experimental determinations, but the discrepancy is probably due to the effect of the phosphorous acid on the velocity of reaction (1) and the agreement is better when the quantity of phosphorous acid is diminished. The addition of iron or copper salts causes a marked increase of the velocity of the reaction, a result in

accord with the observations of Price on the increase of the velocity of reactions (1) by such addition, which was further found to be without effect on reaction (2). The effect of change of concentration of the various constituents or of the change of temperature was also investigated, and the forms of the curves obtained were found to agree closely with those calculated by the author's expressions. L. M. J.

Velocity and Nature of the Reaction between Bromine and Oxalic Acid. THEODORE W. RICHARDS and WILFRED NEWSOME STULL (*Zeit. physikal. Chem.*, 1902, 41, 544--559).—The reaction between bromine and oxalic acid, which proceeds rapidly at high temperatures, was found to take place also in the cold and to be complete. The velocity of the reaction was found to increase with increasing concentration of oxalic acid until a concentration of about 3 per cent., and afterwards to decrease; the values, however, between the concentrations of 1 per cent. and 5 per cent. are very nearly constant. The addition of acids causes a decrease of velocity, and this is especially marked for hydrobromic acid, the effect of which is ten times as great as the effect of hydrochloric acid. Neutral salts or alkalis, however, cause a great increase, and it appears most probable, therefore, that the action takes place between the bromine ions and $C_2O_4^{''}$ ions of the oxalate. The main action, hence, is represented by $C_2O_4^{''} + Br_2 \rightleftharpoons 2CO_2 + 2Br'$; this is, however, complicated by auxiliary reactions as, for example, $H' + Br' \rightleftharpoons HBr$ and $Br' + Br_2 \rightleftharpoons Br'_3$.
L. M. J.

Decomposition of Carbamide. CHARLES EDWARD FAWSITT (*Zeit. physikal. Chem.*, 1902, 41, 601--629).—The formation of ammonium carbonate from carbamide is not due to a direct hydrolysis, but is dependent on the formation of ammonium cyanate which is then hydrolysed, and is hence a purely secondary reaction; it is not reversible. The formation of ammonium cyanate is a reaction of the first order, and the velocity is increased by neutral salts and decreased by ammonium salts; acids cause a great increase of velocity. The equilibrium of carbamide and cyanate is only slightly affected by rise of temperature, the quantity of cyanate being increased. L. M. J.

The Triple Point. PAUL SAUREL (*J. Physical Chem.*, 1902, 6, 399--409).—A mathematical discussion of the equilibrium of the univariant systems which meet at the triple point. L. M. J.

A Theorem of Tammann. PAUL SAUREL (*J. Physical Chem.*, 1902, 6, 410--416).—An extension of a theorem of Tammann relating to a one component system to the multiple point of an n -component system. L. M. J.

Condition Diagram of Phenol. GUSTAV TAMMANN (*Ann. Physik.*, 1902, [iv], 9, 249--270).—As a solid, phenol may exist in one or other of two forms, and the author has determined the conditions of stable existence for each. If ordinary phenol crystals are subjected to

a pressure of 2500 kilos. per sq. cm. at a temperature between 0° and 40° , a contraction and formation of denser crystals takes place, the pressure gradually falling to that value at which both forms can exist together. Similarly, when the pressure on a mass of the denser crystals is gradually diminished, a point is reached at which the crystals, being unstable under the prevailing conditions, are suddenly transformed into the other variety, with marked expansion and rise of pressure. The triple point in the p - T diagram, at which phenol I and phenol II are in equilibrium with liquid phenol, lies at $t = 62.4^{\circ}$ and $p = 2024$ kilos. per sq. cm. From this point, three curves start, two being melting point curves and one a transition curve. The equation for the phenol I melting point curve is $t = 40.5 + 0.0143p - 0.00000173p^2$; that for the phenol II melting point curve is $t - 62.4 = 0.0162(p - 2024)$, this curve being a straight line in the vicinity of the triple point. Above 50° , dT/dp on the transition curve becomes very large, and it is possible that at a certain point it has the value ∞ —a result which would be comparable with that obtained in a study of the mutual relations of the various crystalline forms of ice (*Ann. Physik.*, 1900, [iv], 2, 1). At a point just below 20° , the transition curve divides into two branches, and the field in which phenol I is stable is separated from the corresponding field for phenol II by a zone in which both forms are stable, and which gradually widens with falling temperature. This is a case of 'false' or 'pseudo'-equilibrium, and, along with the parallel observations for ice (*loc. cit.*) and silver iodide (*Abstr.*, 1899, ii, 635), is regarded as experimental evidence in favour of Duhem's views.

The author thinks that earthquakes and the phenomena of volcanic action may be attributed to the liberation of energy accompanying the transition of crystallised substances present in the earth's crust into more stable forms.

J. C. P.

Cause of the Catalytic Action of the Hydrogen Ions of Acids on Hydrolytic Reactions. PAUL ROHLAND (*Zeit. physikal. Chem.*, 1902, 41, 739—740).—The author points out that a hypothesis relating to the above subject and recently brought forward by Noyes and Sammet (*Abstr.*, 1902, ii, 498) was previously suggested by himself (*Abstr.*, 1901, ii, 152).

J. C. P.

History of the Nature of Radicles. FERD. HENRICH (*Ber.*, 1902, 35, 3426—3428).—Controversial, in reply to Vorländer (*Abstr.*, 1902, ii, 496).

T. M. L.

Lavoisier's Laboratory Note-books. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 135, 549—557). Lavoisier's Four Laboratory Note-books. The Second Volume supposed to be lost, but recently recovered. H. BROCARD (*Compt. rend.*, 1902, 135, 574—575).—Brocard has discovered in the *Catalogue général des Manuscrits des Bibliothèques publiques de France* that the second volume of Lavoisier's note-books is in the possession of the Library of Perpignan, to which it was presented by Arago. The period covered

extends from 9th September, 1773, to 5th March, 1774, and includes the results of experiments on oxidation, salt formation, and other subjects.
J. McC.

Inorganic Chemistry.

Hydrogen Tetroxide and Ozonic Acid. A. BACH (*Ber.*, 1902, 35, 3424—3425).—The ozonic acid of Baeyer and Villiger (*Abstr.*, 1902, ii, 650) is identical with the hydrogen tetroxide postulated by the author (*Abstr.*, 1900, ii, 470), whilst the substance which they obtained by the action of ozone on potassium hydroxide is probably not potassium tetroxide but the acid salt KHO_4 . T. M. L.

Purification of Potable Water. P. GUICHARD (*Bull. Soc. chim.*, 1902, [iii], 27, 941—943).—The organic matter present is destroyed by addition of calcium permanganate, the excess of the reagent being removed by allowing the water to flow over metallic iron. The precipitated oxides are then filtered out in a press lined with sterilised paper, which also acts as a mordant to the ferrous carbonate in solution and so requires frequent renewal. T. A. H.

Iodine Pentafluoride. HENRI MOISSAN (*Compt. rend.*, 1902, 135, 563—567).—When fluorine is passed over dry iodine, *iodine pentafluoride* is formed as a colourless liquid which solidifies at 8° . The solid has the appearance of camphor; it boils without decomposition at 97° , but when heated to between 400° and 500° it suffers decomposition and free iodine is obtained; it has not yet been ascertained whether it dissociates into iodine and fluorine or into iodine and another iodine fluoride. Sulphur, phosphorus, arsenic, antimony, and carbon react on the pentafluoride in the cold, as also do the alkali metals; chlorine and bromine only react with it when warmed. It is completely decomposed by water into iodic acid and hydrogen fluoride. Silica and many metallic silicides are attacked by the pentafluoride. It reacts energetically with carbides; the reaction with nitric acid is slow, but with hydrochloric acid violent. Solutions of the alkalis easily decompose it, and when dropped into turpentine the hydrocarbon inflames.

J. McC.

Perchloric and Periodic Acids. A. ASTRUC and H. MURCO (*Bull. Soc. chim.*, 1902, 27, [iii], 929—930).—Perchloric acid behaves as a monobasic acid when titrated in presence of the indicators helianthin, phenolphthalein, Poirrier's blue, litmus, and rosolic acid, whilst periodic acid is monobasic only in presence of helianthin; the basicity of the latter acid, as shown by the other indicators, varies with the alkali used. Similar differences are shown by the heats of neutralisation of the two acids.

T. A. H.

Formation of Dithionic Acid. JULIUS MEYER (*Ber.*, 1902, 35, 3429—3430. Compare Antony and Lucchesi, *Abstr.*, 1899, ii, 299; Antony and Manasse, *Abstr.*, 1899, ii, 753; Antony, *Abstr.*, 1902, ii, 651).—Dithionates are not produced by the action of normal or acid sulphites or of sulphurous acid on ferrous sulphate or manganous sulphate, this being equivalent to the action of sulphuric acid or a sulphate on the corresponding sulphite. T. M. L.

Electrolysis of Fused Sodium Hydroxide. MAX LE BLANC and J. BRODE (*Zeit. Elektrochem.*, 1902, 8, 697—707 and 717—729).—When sodium hydroxide is fused in a nickel crucible and electrolysed with small nickel electrodes, two decomposition points are observed. The first, at about 1·3 volts, corresponds with the evolution of hydrogen and oxygen at the electrodes; the second, at about 2·2 volts, with the formation of metallic sodium at the cathode and the evolution of oxygen at the anode. Anything which tends to eliminate the small quantities of water contained in the fused sodium hydroxide causes the first decomposition point to become less marked: for example, prolonged heating or addition of sodium. Examination of the separate electrode potentials shows that there is only one decomposition point at the anode (discharge of hydroxyl ions), whilst there are two at the cathode (discharge of hydrogen and of sodium ions).

Quantitative measurements of the products of electrolysis show that the yield of oxygen per ampere hour is never quantitative, but that it increases with rising current density. The yield of hydrogen with *E.M.F.*'s less than 2·2 volts is quantitative, provided that no free sodium is present. Free sodium absorbs part of the hydrogen forming the hydride. In completely dry fused sodium hydroxide, sodium alone is formed with *E.M.F.*'s exceeding 2·2 volts. It is proved that neither sodium hydride nor hydrogen is produced. From this, it follows that pure fused sodium hydroxide contains no hydrogen ions (and therefore also no O'' ions), but only the ions Na^+ and OH^- .

Fused sodium hydroxide rapidly attains equilibrium with the aqueous vapour in the surrounding air, and therefore in ordinary circumstances contains an appreciable quantity of water. The dried liquid is therefore hygroscopic and little or no water is evolved at the anode when it is electrolysed. From fused sodium hydroxide to which excess of sodium has been added, small quantities of hydrogen are evolved along with oxygen at the anode, proving that water has been formed there. T. E.

Decomposition of Ammonium Nitrite. ARTHUR A. BLANCHARD (*Zeit. physikal. Chem.*, 1902, 41, 681—708).—The decomposition of ammonium nitrite in concentrated solutions may, as Wegscheider has shown (*Abstr.*, 1901, ii, 384), be represented as follows: $NH_4^+ + NO_2^- = 2H_2O + N_2$, and the author has studied the manner in which the rate of decomposition is affected by the presence of other substances and ions. The only agents which accelerate decomposition are hydrogen ions and free nitrous acid. The presence of acid involves a secondary reaction, in which nitric oxide is liberated, but the primary decomposition of nitrite is found to be independent of this. The gas evolved in the decomposition of the nitrite contains

no nitrous oxide. The rate of decomposition is proportional to the concentration of NH_4^+ and NO_3^- , but it is probable that two independent processes go on simultaneously, each resulting in the liberation of nitrogen. The accelerating effect of nitrous acid has led to a determination of its affinity constant, and the value found (0.0004) agrees well with that arrived at by Schumann (*Ber.*, 1900, 33, 532) from conductivity experiments.

It is pointed out that, in Arndt's recent paper on the above subject (*Abstr.*, 1902, ii, 64), an error was made in referring the quantity of gas evolved to equal quantities of the nitrite instead of to equal volumes of solution.

J. C. P.

Preparation of Calcium. OTTO RUFF and WILHELM PLATO (*Ber.*, 1902, 35, 3612—3619).—The fluoride, chloride, bromide, and iodide of calcium melt at 1330° , 780° , 765° , and 740° respectively, a mixture of 100 parts of the chloride with 16.5 parts of the fluoride melts at 660° and is employed in the electrolytic production of pure calcium. The fused product is heated in a porcelain or carbon crucible and electrolysed with a current of 8 amperes and 8 volts; the anode is a rod of gas carbon, whilst the cathode is a thin iron wire dipping about 2 mm. below the surface of the fused salts and coiled round a thick iron wire which is placed immediately above the liquid. The liberated calcium collects in spherical aggregates round the thin iron wire and is shaken off from time to time. This preparation may be made on a large scale by the aid of the apparatus figured in *Annalen*, 1901, 320, 231, using a direct or an alternating current of 45 amperes and 60 volts.

G. T. M.

Process for Obtaining Metallic Calcium. WILHELM BORCHERS and LORENZ STOCKEM (*Zeit. Elektrochem.*, 1902, 8, 757—758).—The electrolytic apparatus is formed of a cylinder of carbon closed below by means of a water-cooled, metallic, cylindrical box which is insulated from the carbon cylinder by fire-clay. The carbon cylinder is used as anode, the cathode being an iron rod connected with the water-cooled bottom. A layer of powdered fluor spar is first pressed into the apparatus, which is then filled with calcium chloride. The latter is fused by passing an electric current between the electrodes through small carbon rods which are removed as soon as fusion begins; electrolysis then takes place, and at a low red heat spongy calcium is deposited on the cathode. By pressing the sponge together under the fused electrolyte, it can be obtained with a content of 90 per cent. of metallic calcium. If the fused mass is allowed to solidify, a layer of red, dichroic crystals is found surrounding the metallic calcium. These appear to have the composition CaCl .

T. E.

Electrolytic Separation of Pure Strontium. WILHELM BORCHERS and LORENZ STOCKEM (*Zeit. Elektrochem.*, 1902, 8, 759).—Strontium is obtained by the electrolysis of the chloride in an apparatus similar to that used in the preparation of calcium (preceding abstract). The metal is, however, obtained in the form of fused globules, which are almost of the same specific gravity as the fused salt. By arranging

the apparatus with a depression in the bottom, it was possible to collect a quantity of the metal under the electrolyte. Both strontium and calcium are white metals as soft as lead.

T. E.

The Chemical Equation for Reduction by Calcium Carbide. B. NEUMANN (*Zeit. Elektrochem.*, 1902, 8, 772—775).—The equation given by Kügelgen (*Abstr.*, 1901, ii, 98 and 448) cannot be correct since it represents the gas evolved by the reaction as consisting entirely of carbon dioxide, whereas it really contains approximately equal volumes of carbon monoxide and dioxide. The author maintains the accuracy of the equation $3M_2O + CaC_2 = 3M_2 + CaO + 2CO$, and regards the presence of carbon dioxide in the gaseous product as being due to a secondary reaction between the metallic oxide and carbon monoxide.

T. E.

Radium and Radioactive Substances. FRITZ GIESEL (*Ber.*, 1902, 35, 3608—3611).—The flame spectrum of radium differs from its spark spectrum in containing two intense broad lines in the orange-red, whereas the latter spectrum has only faint lines in this region.

Radium bromide, containing barium, evolves bromine, the liberation of the halogen being accompanied by the formation of radium hydroxide, and ultimately of radium carbonate, formed by the action of atmospheric carbon dioxide. The reaction is also attended by the evolution of a permanent gas; this product, which does not explode with oxygen, is extremely radioactive, promotes phosphorescence, and colours the gas pipette in which it is contained. Radium bromide, obtained in a highly purified state by fractional crystallisation, has a beautiful blue phosphorescence and furnishes a continuous spectrum.

In addition to easily absorbed rays, the author's polonium also emits penetrative rays which are deflected in the magnetic field. This radiation, which is rendered apparent by a barium platinocyanide screen, slowly decreases, but exhibits a residual activity (compare Marckwald, *Abstr.*, 1902, ii, 508).

The active rays emitted by the author's polonium correspond with those derived from radium and also from Marckwald's polonium in their behaviour towards a gelatin zinc sulphide screen. This screen is a convenient instrument to employ for detecting easily absorbed rays, and in this way Rutherford's rays have been detected in feebly radioactive impurities obtained in the purification of radium.

G. T. M.

Zinc Oxide. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1902, [vii], 27, 26—66. Compare *Abstr.*, 1902, ii, 322, 489, 549, 606).—A detailed account of work already published, containing also a summary of the results of earlier investigators.

G. T. M.

Crystals formed in the Leclanché Cell. F. M. JAEGER (*Ber.*, 1902, 35, 3405—3407).—Reinvestigation of the crystals which are formed in a Leclanché cell show that they are crystallographically identical with those of the compound $ZnCl_2 \cdot 2NH_3$, first described by

Marignac. Priwoznik's view (*Ber.*, 1876, 9, 612) as to the nature of these crystals is thus confirmed.

K. J. P. O.

Anhydrous Cuprammonium Sulphates. ALBERT BOUZAT (*Compt. rend.*, 1902, 135, 534—536).—In addition to the compounds of copper sulphate and ammonia already known, the author has isolated a bluish-violet compound, $\text{CuSO}_4 \cdot 4\text{NH}_3$, the dissociation pressure of which becomes equal to atmospheric pressure at about 90° . The heats of formation from anhydrous cupric sulphate and gaseous ammonia were determined by dissolving the compounds in excess of ammonia solution with the following results: $\text{CuSO}_4 \cdot \text{NH}_3 + 23.49 \text{ Cal.}$, $\text{CuSO}_4 \cdot 2\text{NH}_3 + 43.22 \text{ Cal.}$, $\text{CuSO}_4 \cdot 4\text{NH}_3 + 73.72 \text{ Cal.}$, $\text{CuSO}_4 \cdot 5\text{NH}_3 + 88.2 \text{ Cal.}$ For a given proportion of ammonia, the heats of formation and tensions of dissociation correspond closely with those of the cuprammonium chlorides (*Abstr.*, 1902, ii, 607).

C. H. B.

Thallic Sulphates and Double Sulphates. HUGH MARSHALL (*Proc. Roy. Soc. Edin.*, 1902, 24, 305—311. Compare Locke, *Abstr.*, 1902, ii, 497, and Piccini and Fortini, *ibid.*, 607).—It has not been possible to obtain any indication of the formation of an alum containing thallium as the triad metal. Thallic sulphate readily forms a basic salt of the formula $\text{OH} \cdot \text{TlSO}_4 \cdot 2\text{H}_2\text{O}$. After adding ammonium sulphate to a solution of this basic salt, a granular precipitate of an anhydrous double salt, $\text{NH}_4\text{Tl}(\text{SO}_4)_2$, separates. When recrystallised from dilute sulphuric acid, monoclinic, prismatic crystals of $\text{NH}_4\text{Tl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ separate. A solution of the double sulphate, when saturated with ammonium sulphate, deposits fine needles of $(\text{NH}_4)_3\text{Tl}(\text{SO}_4)_3$. Potassium thallic sulphate, $\text{OH} \cdot \text{TlK}_2(\text{SO}_4)_2$, has been obtained; when heated, it darkens, then again becomes white. A nitric acid solution of it deposits crystals of $\text{KTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Rubidium thallic sulphate separates either as a granular anhydrous salt, $\text{RbTl}(\text{SO}_4)_2$, or as the hydrated salt, $\text{RbTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, depending on the temperature and the acid concentration of the solution.

In an attempt to prepare thallic sulphate by electrolysis, a light yellow, crystalline powder of thallic sulphate, $\text{Tl}'_5\text{Tl}''(\text{SO}_4)_4$, was obtained. By mixing thallic and thallic sulphates in solution in molecular proportion, small crystals of $\text{Tl}'\text{Tl}''(\text{SO}_4)_2$ were formed which show strong double refraction and appear to be rhombic.

J. McC.

New Reaction for Manganese, Nitrates, Chlorates, Lead Peroxide, &c. Composition of Perchlorides of Lead and Manganese. LUCIEN L. DE KONINCK (*Chem. Centr.*, 1902, ii, 14; from *Bull. assoc. belg. Chimistes*, 16, 94—98).—When one or two drops of nitric acid of sp. gr. 1.35—1.40 are added to a boiling solution of a manganese salt in fuming hydrochloric acid, the colour of the liquid changes to a very dark green with a tinge of yellow, owing to the formation of manganese tetrachloride or possibly of a chloromanganic acid, H_2MnCl_6 . This compound is very stable in hydrochloric acid; the coloration disappears on dilution, but is only destroyed

by prolonged boiling. A solution of manganous chloride containing 0.001 gram of manganese in 1 c.c. is used for the purpose of the test. In addition to nitric acid, nitrates, chlorates, hypochlorites, chromates, and lead dioxide also give the reaction, whilst sodium bromate, potassium perchlorate, sodium peroxide, bromine, potassium persulphate, red lead, and sodium nitrite do not. It is remarkable that of the latter compounds sodium bromate and sodium nitrite cannot therefore form chlorine when treated with hydrochloric acid. By the action of hydrochloric acid on red lead, lead tetrachloride is supposed to be formed, but its exceptional behaviour would be more in accordance with the formation of a trichloride, PbCl_3 . On this hypothesis, by the action of hydrochloric acid on red lead, the trichloride, dichloride, and water would be formed, whilst lead dioxide and hydrochloric acid would yield lead trichloride, chlorine, and water. Possibly, however, a reversible double decomposition between lead tetrachloride and manganous chloride may take place and this would account for the decolorisation of the manganese solution, its coloration by lead dichloride, and also for the fact that the colour is formed when red lead is treated with a saturated solution of manganous chloride in hydrochloric acid.

E. W. W.

New Cobalt Silicide. PAUL LEBEAU (*Compt. rend.*, 1902, 135, 475—477. Compare *Abstr.*, 1901, ii, 242).—A cobalt silicide, CoSi_2 , is obtained by heating cobalt with an excess of silicon, or a mixture of cobalt, silicon, and copper silicide, in the electric furnace. It forms dark crystals with a bluish reflection, which often have an octahedral form and seem to belong to the cubic system. It has a sp. gr. 5.3 and hardness between 4 and 5. It is attacked by fluorine, with incandescence, if gently heated, by chlorine at 300° , and by bromine and iodine at a dull red heat. Sulphur has no action on it at the softening point of glass, oxygen attacks it superficially at 1200° , and nitric and sulphuric acids, concentrated or dilute, are without action. Hydrochloric acid, when concentrated and boiling, attacks the silicide slowly, and hydrofluoric acid dissolves it rapidly; hot concentrated solutions of alkali hydroxides attack it slowly, but the fused hydroxides decompose it rapidly.

C. H. B.

Preparation of Pure Iron. A. SKRABAL (*Ber.*, 1902, 35, 3404—3405).—Extremely pure iron was prepared by depositing iron electrolytically from ferrous ammonium oxalate on platinum foil; the electrode so prepared was immersed as anode in a solution of ferrous sulphate acidified with sulphuric acid and electrolysed, using a very small *E.M.F.* (0.4 volt). The iron thus obtained was crystalline in structure and pure white; it dissolved slowly but completely in dilute sulphuric acid, odourless hydrogen being evolved.

K. J. P. O.

Aluminium Chromate. MAX GRÖGER (*Ber.*, 1902, 35, 3420—3424).—Addition of aqueous potassium chromate to a solution of potassium alum precipitates basic aluminium sulphates; as the quantity of the chromate is increased, the precipitate becomes mixed

with an increasing amount of chromate; when the alum and potassium chromate are in the ratio of $\text{Al}_2\text{O}_3 : 2\text{CrO}_3$, no precipitate is formed. On mixing solutions of aluminium chloride and potassium chromate, a yellow precipitate is formed which has the composition $2\text{Al}_2\text{O}_3 \cdot \text{CrO}_3 \cdot 6\text{H}_2\text{O}$; the precipitation of the aluminium is not complete until 3 mols. of potassium chromate have been added for each mol. of aluminium chloride.

Solutions made by dissolving aluminium hydroxide in chromic acid always contain Al_2O_3 and CrO_3 in the proportion of 1 : 1.4—1.45; from this solution, the insoluble basic chromate mentioned above separates on keeping. No indication was observed of the formation of the compound $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3 \cdot 7\text{H}_2\text{O}$, described by Fairrie (this Journal, 1851, 4, 301.)

K. J. P. O.

Existence of Colloidal Tungstic Acid. Interaction of Hydrochloric Acid and Sodium Tungstate. NICOLA PAPPADÀ (*Gazzetta*, 1902, 32, ii, 22—28).—When moderately concentrated hydrochloric acid is added drop by drop to a 5 per cent. solution of sodium tungstate, a white, gelatinous precipitate is formed when the liquids meet, but quickly goes into solution, yielding an acid liquid. The author confirms Graham's statement (*Proc. Roy. Soc.*, 1864) that the solution contains colloidal tungstic acid, Sabanéeff's assumption that a metatungstate of the composition $\text{Na}_2\text{O} \cdot 4\text{WO}_3$ is formed being incorrect.

For preparing a solution of colloidal tungstic acid, the following method is recommended. To a concentrated sodium tungstate solution, hydrochloric acid is added until the liquid has an acid reaction, the white, gelatinous precipitate thus obtained being washed several times by decantation at low temperatures (0—5°); during these operations, the precipitate is protected from currents of air, which would produce a change in the colloid. Fifteen parts of the acid are then carefully dissolved by gentle warming with a concentrated solution of 1 part of oxalic acid, and the liquid subjected to dialysis. If the outer water is frequently changed, the oxalic acid is completely removed, leaving a colloidal solution of tungstic acid which may be concentrated in a vacuum over sulphuric acid at the ordinary temperature until it contains as much as 1.25 per cent. of WO_3 .

T. H. P.

Potassium-Tungsten Bronze. GEORG VON KNORRE and E. SCHÄFER (*Ber.*, 1902, 35, 3407—3417. Compare Abstr., 1883, 650).—Hallopeau (Abstr., 1899, ii, 32, 555) has stated that the potassium-tungsten bronze, obtained by reducing potassium paratungstate with hydrogen, has the formula $\text{K}_2\text{W}_3\text{O}_9$, whilst that prepared by reduction of the molten tungstate with tin has the formula $\text{K}_2\text{W}_5\text{O}_{15}$. The authors found previously (*loc. cit.*) that only one such bronze existed, and that its composition was expressed by the formula $\text{K}_2\text{W}_4\text{O}_{12}$. As a result of a full investigation of the bronze, prepared by both methods, it is found that their former view is entirely confirmed.

K. J. P. O.

Preparation and Properties of a New Vanadium Silicide. HENRI MOISSAN and ALFRED HOLT (*Compt. rend.*, 1902, 135, 493—497. Compare Abstr., 1902, ii, 610).—Besides the vanadium silicide, VSi_2 ,

previously prepared, another, of the formula V_2Si , can be obtained (1) by heating a mixture of 120 parts of vanadium trioxide and 14 parts of silicon in the electric furnace with a current of 1000 amperes at 50 volts; (2) by the action of silicon on vanadium carbide, namely, by heating a mixture of vanadium trioxide, silicon, and carbon for 4 minutes with a current of 500 amperes at 50 volts; and (3) by heating a mixture of vanadium trioxide, silicon, and copper in the electric furnace. The silicide is obtained in brilliant prisms which have a metallic lustre and a sp. gr. of 5.48 at 17°. It fuses at a temperature superior to the melting point of the disilicide, and is insoluble in water, alcohol, ether, or benzene; fluorine does not attack it in the cold; with chlorine at a red heat, it gives vanadium tetrachloride and silicon tetrachloride, and with bromine, vanadium tribromide and silicon hexabromide. It is only superficially attacked by water, sulphur, or hydrogen sulphide at a high temperature, and ammonia has no action on it. It burns when heated in hydrogen chloride. When fused with excess of silicon, it gives the disilicide. It is decomposed by molten sodium or copper, but is hardly affected by silver. Hydrochloric, nitric, or sulphuric acids do not attack it, but a mixture of nitric acid with either of the others dissolves it, and it is easily attacked by hydrofluoric acid, even in dilute solution. It is also decomposed by fused potassium hydroxide or a mixture of potassium carbonate and nitrate. J. McC.

Double Nitrites of Iridium. ÉMILE LEIDIÉ (*Bull. Soc. chim.*, 1902, 27, [iii], 936—940).—Iridium potassium nitrite, $Ir_2K_6(NO_2)_{12}$, prepared by the addition of potassium nitrite to a solution of iridium sulphate warmed to 70—80°, is a white powder which dissolves readily in boiling water, less so in cold, and is insoluble in potassium chloride solution. It decomposes at 450°, forming potassium hexairidite, and at a red heat is converted into potassium dodecairidite. Hydrochloric and sulphuric acids decompose the salt with the formation of potassium chloroiridate and iridium sulphate respectively. When potassium nitrite is added to solutions of potassium chloroiridite, the precipitate obtained varies in composition, and in no circumstances is the true double nitrite thus produced (compare Gibbs, *Ber.*, 1871, 4, 280, and Lang, *K. Vet.-Akad. Handl.*, 5, vii, 7).

Iridium sodium nitrite, $Ir_2Na_6(NO_2)_{12} \cdot 2H_2O$.—The author was unable to obtain the compounds of this salt with sodium chloroiridite described by Gibbs and by Lang (*loc. cit.*).

Iridium ammonium nitrite, $Ir_2(NH_4)_6(NO_2)_{12}$, prepared by the addition of sodium nitrite and ammonium sulphate to a warm solution of iridium sulphate, is a white powder with properties similar to those of the potassium salt. It evolves nitrogen when boiled with water and detonates when heated. The double nitrites of iridium with silver, mercury, and cobalt described by Gibbs and by Lang (*loc. cit.*) were not obtained. T. A. H.

Iridium and its Compounds. ARTURO MIOLATI and C. GIALDINI (*Atti R. Accad. Lincei*, 1902, [v], 11, ii, 151—158).—The authors,

like Leidić (Abstr., 1901, ii, 62), are unable to confirm the formulae given by Gibbs (*Ber.*, 1871, 4, 280) and by Lang for the double nitrites of iridium. For the compound described by Lang as having the composition $\text{Ir}_4(\text{NO}_2)_{18}\text{Cl}_6\text{K}_{12}$, and which Leidić only obtained in the form of a lake containing considerable proportions of potassium chloride, the authors have obtained analytical results agreeing moderately well with the formula $\text{IrCl}_3(\text{NO}_2)_3\text{K}_3$.

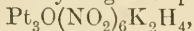
Potassium dinitrotetrachlorosesqui-iridate, $\text{IrCl}_4(\text{NO}_2)_2\text{K}_3$, prepared by treating ammonium chloroiridate, suspended in water, with nitrogen trioxide and adding to the concentrated solution the theoretical quantity of potassium chloride solution, forms golden-yellow crystals very soluble in water. A small quantity of a crystalline, red powder was also formed, but was not further investigated. With hydrochloric acid, potassium dinitrotetrachlorosesqui-iridate is converted into chloroiridate, whilst when boiled with potassium nitrite solution it yields Lang's compound, $\text{IrCl}_3(\text{NO}_2)_3\text{K}_3$ (?), previously mentioned. The analysis of this compound was carried out by first converting it into chloroiridate by repeated evaporation with hydrochloric acid on the water-bath, and then igniting this in a current of hydrogen until the weight is constant; the potassium chloride and iridium thus obtained are then extracted with water and the residual iridium ignited in a stream of hydrogen and finally weighed. Special stress is laid on the use of hydrogen, since the authors find that when iridium is heated in the air it loses 4--5 per cent. of its weight. The *cæsium* salt, $\text{IrCl}_4(\text{NO}_2)_3\text{Cs}_3$, the *silver*, *thallium*, *mercuric*, and *basic lead* salts, $[\text{IrCl}_4(\text{NO}_2)_3]_2\text{Pb}_3 \cdot 2\text{Pb}(\text{OH})_2$, were prepared and analysed. T. H. P.

Complex Platinum Salts. Reactions of Platoso-oxalonitrites. MAURICE VÉZES (*Bull. Soc. chim.*, 1902, 27, [iii], 930—936. Compare Abstr., 1899, i, 671 and 741; 1901, i, 187).—When chlorine is passed through a warm aqueous solution of potassium platoso-oxalonitrite, $\text{PtCl}_2\text{O}_4(\text{NO}_2)_2\text{K}_2 \cdot \text{H}_2\text{O}$, there is formed eventually potassium platinichloride, and probably as an intermediate product potassium platosodichloronitrite, $\text{PtCl}_2\text{NO}_2\text{K}_2$. The action by which the platoso-oxalonitrite is formed (*loc. cit.*) is therefore irreversible. Bromine and iodine react in an analogous manner.

Hydrochloric acid also furnishes potassium platinichloride together with oxalic acid and nitric oxide. Hydrobromic and hydriodic acids react similarly, the latter producing platinum tetraiodide, potassium oxalate, and nitric oxide. The addition of ammonia to aqueous solutions of potassium platoso-oxalonitrite gives an immediate crystalline precipitate of platosamine nitrite, $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$.

Silver potassium platoso-oxalonitrite, $\text{Pt}(\text{C}_2\text{O}_4)(\text{NO}_2)_2\text{AgK} \cdot \text{H}_2\text{O}$, produced by the admixture of solutions of silver nitrate and the potassium salt, forms monoclinic crystals [$a:b:c = 0.8820:1:1$; $\beta = 87^\circ 52'$]. Its solubilities in boiling and cold water are 2 and 0.01 per cent. respectively. At 100° it becomes anhydrous, and at 250° decomposes, leaving potassium nitrate mixed with metallic silver and platinum. With cupric chloride, potassium platoso-oxalonitrite gives a precipitate of copper oxalate, and from the filtrate potassium platoso-dichloronitrite

can be obtained; with cupric sulphate or nitrate there is produced copper oxalate and potassium hydrogen triplatoso-hexanitrite,



(Abstr., 1893, ii, 213). Haloid salts of nickel, lead, and magnesium react in a manner analogous to that of cupric chloride and thus furnish a ready means of obtaining derivatives of the type



where X is a halogen element.

T. A. H.

Mineralogical Chemistry.

Melting Points of Minerals and Rocks. CORNELIUS DOELTER (*Tsch. Min. Mitth.*, 1902, 21, 23—30. Compare Abstr., 1898, ii, 383). —The values previously obtained by the same author (*ibid.*, 1901, 20, 210—232) in a gas-furnace are too low; the following new determinations were made in an electric furnace:

Melanite.....	920°	Oligoclase	1120°
Ægirite	925	Labradorite	1125
Lepidolite	930	Biotite.....	1130
Gastaldite	1025	Anorthite	1132
Hornblende (containing much iron)	1065	Sanidine	1130
Elæolite	1080	Microcline	1155
Augite (from Sasbach) ...	1085	Meionite.....	1155
Hornblende (containing little iron)	1085	Orthoclase	1175
Zoisite.....	1090	Magnetite	1185
Epidote	1090	Hypersthene	1185
Garnet (from Traversella)	1090	Muscovite	1230
Augite (from Arendal) ...	1095	Actinolite	1230
Nepheline	1095	Wollastonite ..	1220
Diallage	1095	Meroxene	1235
Grossular	1110	Pleonaste	1240
Albite.....	1110	Leucite	1300
		Olivine	1350
		Bronzite	1400

	Softens.	Fluid.
Granite from Predazzo	1160°	—
Monzonite from Predazzo	1125	1190°
Lava from Vesuvius.....	1060	1090
Lava from Etna	970	1040
Basalt from Remagen	1020	1075
Limburgite from Kaiserstuhl	1000	1060
Phonolite from Brück	1060	1090
Nepheline-syenite from St. Vincent	1060	1100

L. J. S.

Microchemical Reactions of Certain Minerals. JOHANN LEMBERG (*Zeit. Kryst. Min.*, 1902, 36, 657—658; from *Zeit. Deutsch. geol. Ges.*, 1900, 52, 488—496. Compare Abstr., 1896, ii, 430).—Details are given of the action of aqueous solutions of various reagents, such as potassium cyanide, potassium hydroxide, sodium sulphide, ammonia, sodium carbonate, lead nitrate, &c., on various minerals; the differences in the observed reactions are often useful for purposes of discriminating between certain minerals.

L. J. S.

Libollite. JACINTO PEDRO GOMES (*Jahrb. Min.*, 1902, ii, Ref. 234; from *Comm. Direc. Serviços Geol. Portugal*, 1901, 4, 206—207. Compare Abstr., 1900, ii, 86).—A description is given of new material from Cambulo (Cambambe), prov. Angola, Portuguese West Africa, which occurs as veins in schistose greywacke conglomerate.

It is pointed out by the abstractor, V. de SOUZA-BRANDÃO, that the composition, $C_{23}H_{23}O_2$, of libollite is very nearly the same as that of muckite, and that the new name, libollite, thus appears to be superfluous.

L. J. S.

Calcite from the Crimea. PETR A. ZEMJATSCHENSKY (*Zeit. Kryst. Min.*, 1902, 36, 598—605).—A detailed description is given of the mode of occurrence and the characters of scalenohedral and prismatic crystals of calcite from veins and cavities in argillaceous limestone on Mount Čelebi-jaur-n-beli, near Baidar. The following analysis by Kaschinskij shows the material to be almost as pure as Iceland-spar:

CaO.	FeO.	MgO.	CO ₂ .
55·860	0·405	trace	43·78

A less perfectly transparent sample contained: SiO₂, 0·158; MgO, 0·238; FeO, 0·873 per cent.

L. J. S.

Pelagosite. S. SQUINABOL and G. ONGARO (*Jahrb. Min.*, 1902, ii, Ref. 189; from *Rivista Min. Ital.*, 1901, 26, 44).—Analysis of black pelagosite from the island of Tremiti gave:

CaCO ₃ .	MgCO ₃ .	CaSO ₄ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	Soluble SiO ₂ .
87·794	1·628	2·454	0·794	0·476	0·107

Insoluble SiO ₂ .	KCl.	NaCl.	Organic matter.	H ₂ O.	Total.
0·556	0·317	2·185	2·011	1·197	99·519

Sp. gr. 2·835; H. 4. The material has a vitreous lustre and varies in colour from light grey to black; it has a radially fibrous structure. It occurs as an incrustation on calcite, and is being deposited at the present time from sea-water.

G. DE GÜTZEN (*ibid.*, 26, 35) finds that pelagosite is optically uniaxial and negative, and he considers it to be a hard variety of calcite.

L. J. S.

Magnesite in Greece. CONSTANTIN ZENGELIS (*Berg-Huettenm. Zeit.*, 1902, 61, 453—454).—Although magnesite is a mineral of fairly wide distribution, it is not often found sufficiently pure for use as a refractory material for furnace linings, &c. The best is from Eubœa in Greece; this averages 95 per cent. of magnesium carbonate, and sometimes contains more than 99 per cent. It occurs as veins in chalk and serpentine and is often associated with opal and chromite. The following analyses give the composition of material from different localities:

	SiO ₂ .	CaO.	MgO.	CO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ , FeO.	MgCO ₃ .
Mantudi, Eubœa...	0.38	1.68	46.09	51.51	0.15	0.08	96.32
" " ...	1.63	1.44	45.75	49.88	0.17	1.19	95.61
Thebes	1.05	0.91	46.61	51.72	trace	—	97.41
Scenteraga, Lokris	0.29	1.95	45.86	51.56	0.19		95.84
Corinth—Megara .	0.57	0.40	47.06	51.55	0.11	—	98.35
Papades, Eubœa ...	2.68	2.23	43.45	48.72	3.02		90.81

L. J. S.

Anthophyllite from Saint-Germain-l'Herm. GEORGES FRIEDEL (*Bull. Soc. franç. Min.*, 1902, 25, 102—110).—A vein of a greenish, nodular rock penetrates the granite at Saint-Germain-l'Herm. The nodules consist mainly of antigorite with crystals of anthophyllite and scales of talc; they are surrounded by a zone of yellowish, silky fibres of anthophyllite, the fibres being arranged perpendicularly to the surface of the nodules, and are sometimes several centimetres in length. Intermixed with the fibres are sometimes opal, talc, and carbonates of calcium, magnesium and iron, whilst the yellowish colour is due to the presence of oxide of iron; pure material is snow-white or slightly greenish. The mean of three analyses of pure material dried at 100° is:

SiO ₂ .	FeO.	MgO.	CaO.	Al ₂ O ₃ .	H ₂ O.	Total.	Sp. gr.
58.38	8.37	28.82	0.61	0.10	3.43	99.71	3.034

Of the water, 0.68 per cent. is given off at a dull red heat, but the mineral still retains its optical characters; this is therefore called *zeolitic water*. The remainder of the water is expelled at a higher temperature with the complete decomposition of the mineral. Only when the water is included with the bases does the above analysis approximate to the accepted formula, R''O, SiO₂, of anthophyllite.

Crystals of anthophyllite do not break with plane cleavage surfaces, but with a curved surface parallel to the length of the prism. *Cylindrical cleavages* of the same character are possessed by gypsum parallel to the zone-axis [101], and less perfectly parallel to [001].

L. J. S.

[Magnetite, Serpentine and Amphibole from the Southern Urals.] FRANZ LOEWINSON-LESSING (*Zeit. Kryst. Min.*, 1902, 36, 653—654; from *Trav. Soc. Naturalistes, St. Pétersbourg, Sect. Géol. Minéral.*, 1900, 30, 169—256).—Descriptions of several minerals, with

chemical analyses of the following, are given in a geological account of the Jushno-Sausersk estate and of Mount Deneshkin Kamen in the Southern Urals. I, Magnetite, enclosing some pleonaste and orthorhombic pyroxene, occurring as veins in banded gabbro along the Bystraja. II, Serpentine, of a rich green colour and translucent at the edges, from the Jelowki. III, Amphibole (pargasite), of a brown colour, in granulite from the Salaja: this analysis corresponds with the formula $2R'_2R''Si_2O_6 + 3R''R'''_2SiO_6 + 9R''SiO_3$.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	4·26	13·11	49·91	30·86	—	—	3·23	—	—	—	99·40
II.	35·98	3·91	3·76	1·27	—	—	36·83	1·12	0·29	14·77	97·93
III.	43·19	17·77	3·22	9·78	trace	10·01	11·57	3·12	trace	1·05	99·74

L. J. S.

Enclosures of Garnet-Idocrase Rock in the Serpentine of Paringu [Southern Carpathians]. G. MUNTEANU-MURGOCI (*Zeit. Kryst. Min.*, 1902, 36, 649—653; from *Univ.-Diss. München*, 1901; *Bull. Soc. Sci. Bukarest*, 1900—1901, 9, 568—612, 764—831).—The serpentine, an alteration product of an olivine-pyroxene-rock (lherzolite), encloses masses of a granular garnet-idocrase rock, which is an endomorphic contact product of gabbro: there are also silicate-hornfels at the contact of the eruptive rock with limestone. The following mineral analyses are given in a petrographical description of these rocks; I, diallage from the serpentine; Ia, Ib, diallage from the garnet-idocrase rock. II, Antigorite from the serpentine. IIIa, IIIb, Lotrite, a new mineral occurring as greenish veins and patches in clinozoisite-hornfels at the serpentine contact in the Lotru valley. The characters as determined under the microscope are given: the mineral is very similar to prehnite, but differs from this in the higher refraction ($n=1·67$) and lower double refraction ($\gamma-a=0·014$). The composition is very close to that of chlorastolite, and corresponds with the formula $4SiO_2·Al_2O_3·3(Ca,Mg)O·2H_2O$. IV, Grossular; VI, idocrase; and VII, VIIa, clinochlore, from the garnet-idocrase rock. V, Hessonite; and VIa, idocrase, as crystals on the walls of crevices:

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Loss on ignition.	Total.	Sp. gr.
I.	48·15	0·31	2·91	5·84		0·68	19·89	20·28	2·79	100·85	3·28
Ia.	48·47	0·32	3·06	5·14	3·18	0·30	20·15	17·70	2·48	100·80	3·31
Ib.†	47·84	0·31	4·26	3·52	5·98	0·25	22·17	12·33	3·59	100·25	3·232
II.	37·8	—	1·5	4·8	1·7	—	—	38·7	14·8	99·3	2·52
IIIa.	38·02	—	30·90*	—	0·33	—	23·56	2·80	6·24	101·85	3·23
IIIb.‡	39·44	—	28·33*	—	—	—	22·21	3·20	6·58	100·69	3·229
IV.†	33·38	0·40	22·27	2·06	0·54	0·23	32·88	3·07	1·08	100·91	3·48
V.	38·89	trace	13·57	9·78	1·01	0·22	36·34	0·52	0·65	100·98	—
VI.	36·71	0·42	15·60	4·79	1·28	0·23	34·29	3·90	2·88	100·15	3·36
VIa.	37·48	0·26	15·72	5·89	1·30	0·68	32·19	[3·77]	2·71	100·00	—
VII.	30·29	—	16·49	6·20	5·14	trace	trace	28·65	12·70	99·47	—
VIIa.	31·99	—	17·11	2·71	1·54	0·84	—	32·91	12·94	100·04	—

* Including a little Fe₂O₃.

† Also traces of alkalis.

‡ Also Na₂O, 0·93.

L. J. S.

Clays and Loams near Nürnberg. H. KAUL (*Jahrb. Min.*, 1902, ii, Ref. 223; from *Inaug.-Diss. Erlangen*, 1900, 125 pp.).—An account is given of the clays and loams, used for technical purposes, which occur in the neighbourhood of Nürnberg; 20 analyses are given, and the refractory qualities of the materials were determined.

L. J. S.

Clays of Alsace. J. A. KÖRNER (*Jahrb. Min.*, 1902, ii, Ref. 222; from *Inaug.-Diss. Erlangen*, 1900, 52 pp.).—Several of the clays used in Alsace for technical purposes were submitted to microscopical examination and chemical analysis; 14 analyses are given and the analytical methods discussed.

L. J. S.

Physiological Chemistry.

Influence of High Pressure of Oxygen on the Circulation of the Blood. LEONARD E. HILL and JOHN J. R. MACLEOD (*Proc. Roy. Soc.*, 1902, 70, 454—455).—From microscopic observations of the frog's web and bat's wing, the animals being placed in a steel pressure chamber with glass ends, the conclusion is drawn that a rapid increase of pressure up to 70 atmospheres has no mechanical effect on the circulation of the blood. On decompression, gas bubbles are liberated, but on recompression these pass again into solution.

W. D. H.

The Influence of an Atmosphere of Oxygen on the Respiratory Exchange. LEONARD E. HILL and JOHN J. R. MACLEOD (*Proc. Roy. Soc.*, 1902, 70, 455—462).—The influence of an increased amount of oxygen in the air has been investigated by others, but the results obtained have been contradictory. The present experiments were made on mice. In pure oxygen, the amount of carbon dioxide is diminished by from 8 to 40 per cent.; when the animals are put in air again, the amount of carbon dioxide expired rises. The water excreted and the oxygen absorbed are also lessened, but the results are not so constant or marked. This is partly attributed to an increase in the chance of experimental error. The rectal temperature falls in oxygen. Full experimental details of typical experiments are given.

W. D. H.

The Importance of Sodium Chloride in Heart Activity. DAVID J. LINGLE (*Amer. J. Physiol.*, 1902, 8, 75—98).—The experiments were made with strips of the turtle's ventricle which had ceased to contract. The conclusions are that sodium chloride is absolutely necessary to start rhythmic action in them. Agents like caffeine, which intensify rhythmic activity, cannot originate it. What has been described as the sodium chloride arrest of the heart is

probably due to lack of oxygen in the salt solution; oxygen, however, by itself cannot originate the rhythm, but oxygenated salt solution will keep the strips beating as long as a mixture of salt solutions. Oxalate solution that precipitates calcium will permit beats to begin if sodium chloride is present.

W. D. H.

Action of Acids and Acid Salts on Blood Corpuscles and other Cells. S. PESKIND (*Amer. J. Physiol.*, 1902, 8, 99—102).—Small quantities of most acids, and many acid salts, when added to defibrinated blood, agglutinate and precipitate the blood corpuscles. Corpuscles freed from serum are similarly acted on. This is due to an action on the stromata; these are similarly affected in laked blood, even if the laking is done with ether. The effect is therefore not on the lecithin or cholesterol, but on the proteid of the stromata, which is here spoken of as an alkali-globulin. Slight excess of the acid reagent laves the corpuscles, but this may be prevented by previous repeated washings with ice-cold salt solution. More than a slight excess prevents precipitation and agglutination. Leucocytes, yeast cells, bacteria, &c., are similarly affected. A specimen of leucæmic blood examined yielded a serum which contained an *isolysin*, that is, a substance which laves human blood; the serum also precipitated and agglutinated human and dog's red corpuscles.

W. D. H.

Behaviour of Nucleated Red Corpuscles to Hæmolytic Agents. GEORGE N. STEWART (*Amer. J. Physiol.*, 1902, 8, 103—138).—Nucleated red corpuscles take up ammonium chloride in preference to sodium chloride when placed in a mixture of these salts. This, as in the case of non-nucleated corpuscles, does not depend on the life of the corpuscles; the same difference is seen, although it is less in degree in corpuscles which have been hardened by formaldehyde. Saponin produces an increase in the conductivity of the blood, even after previous treatment with formaldehyde. This is not associated with laking, but is due to an increased permeability of the corpuscles to electrolytes. Dilution of the blood with water diminishes its conductivity less than a corresponding dilution of the serum; this is owing to a participation of the corpuscular electrolytes in the conduction after dilution. Heat-laking markedly lessens the conductivity of bird's blood, but not of mammalian blood. Embryonic mammalian corpuscles, the elements of red marrow, and the corpuscles from a case of pernicious anæmia behave like bird's corpuscles, except that heat-laking destroys their nuclei.

Intraglobular crystallisation of the hæmoglobin of *Necturus* blood is readily obtained by the action of various hæmolytic agents; the hæmoglobin cannot exist in the corpuscles in ordinary aqueous solution. If hardened by Hayem's solution, these corpuscles are laked by hydrogen sulphide without swelling of the nucleus. Ammonia swells the nucleus. If such hardened corpuscles are treated with hydrogen sulphide, ammonia, and then Löffler's methylene-blue, an apparent envelope can be demonstrated. If the corpuscles are fixed by osmic acid or by formaldehyde, they swell under the influence of ammonia and heat, whilst the nuclei retain their original size. These facts

indicate the existence of difference in the nature and point of attack of the fixation by different hardening agents. The permeability of the corpuscles for ammonium chloride does not depend on the toxic effect of the salt on the corpuscles.

W. D. H.

Human Pancreatic Juice. O. SCHUMM (*Zeit. physiol. Chem.*, 1902, 36, 292—332).—The number of analyses of human pancreatic juice is small. In pancreatic cysts, the fluid is poor in solids, and some of the pancreatic ferments may be absent; the amylolytic ferment is the most constant. In the present case, the fluid of the cyst contained all three ferments, but more attention is given to the fluid which subsequently flowed from the fistula. It is not nearly so rich in solid as the fresh juice from the dog, but more nearly resembles that obtained from the so-called permanent fistula in that animal. The fluid was thin, slightly cloudy, and deposited on cooling a small amount of a mucin-like substance which gave the proteid reactions. It was strongly alkaline, gave off abundance of carbon dioxide on acidification, and contained some coagulable proteid, but no sugar. It possessed a powerful tryptic, diastatic, fat-splitting, and emulsifying action.

The following table gives the analyses in parts per cent. of human pancreatic juice hitherto published. The fluid obtained by Herter was removed after death in a case of obstruction of the pancreatic duct; the other three are of fluids from a fistula after operation.

Observer.	Water.	Solids.	Ash.	In alcohol.			
				Soluble.		Insoluble.	
				Organic solids.	Ash.	Organic solids.	Ash.
Herter	97.59	2.41	0.62	0.64	0.51	1.15	0.11
Zawadsky	86.41	13.59	0.34	0.83		—	—
Kulmkaupff ...	97.97	2.03	0.81	0.86	—	0.36	—
Schumm	98.47	1.53	0.85	0.56	0.85	0.13	0.005

W. D. H.

Influence of Feeding with Sucrose and Starch Syrup on the Composition of Honey. ED. VON RAUMER (*Zeit. anal. Chem.*, 1902, 41, 333—350).—The author has fed a hive of bees with a solution containing sucrose and starch syrup, and has analysed the honey obtained. From the results, it is concluded that sucrose is to a very large extent converted into invert sugar in the stomach of the bee, so that honey contains only a small proportion of sucrose. A fermentable, non-reducing dextrin present in the starch syrup was also found to be converted into a reducing sugar. Food containing dextrin

cannot for long be used by bees, which after a time become ill and refuse to touch such food.

It is also found that both the non-fermentable and fermentable dextrins occurring in honey are essentially different from those contained in starch syrup, the former possessing a lower specific rotation than the latter.

From a consideration of his own results and of those of other investigators, the author concludes that, when dextrins undergo fermentation by yeast, they are first saccharified by enzymes in the yeast.

T. H. P.

Diuresis. 1. Introduction. WILHELM FILEHNE (*Pflüger's Archiv*, 1902, 91, 565—568). 2. Preliminary Experiments. W. FILEHNE and H. BIBERFELD (*ibid.*, 569—573). 3. The Opposite Influence of Two Salts. W. RUSCHHAUPT (*ibid.*, 574—583). 4 and 5. The Influence of Diuretics on the Excretion of Sodium Chloride. CARL POTOTZKY (*ibid.*, 584—594), W. RUSCHHAUPT (*ibid.*, 595—598). 6. The Influence on Chlorate Excretion by Infusion of Sodium Chloride. WILHELM ERCKLENTZ (*ibid.*, 599—618). 7. The Effect of Certain Operative Procedures on Sodium Chloride Diuresis. W. RUSCHHAUPT (*ibid.*, 619—628). —The studies on diuresis here recorded have an important bearing on the theory of urine formation. Theories on this subject fall under two main headings, the mechanical (Ludwig) and the secretory (Heidenhain). Recent work by Cushny is directed against the latter theory, and the doctrine that reabsorption takes place in the convoluted tubules is supported. Thus he injected sodium sulphate in 'salt-poor' rabbits, and the chlorides excreted were increased threefold; this he attributes to the rapidity with which the urine is washed along the tubules and the consequent lack of time for reabsorption to take place. The arguments in the present series of papers are directed against this idea. It is shown that water introduced into the stomach of such a rabbit acts as a diuretic; nevertheless, the amount of urinary chlorides is still further lessened. Dreser previously pointed out that *urina potus* is hypotonic, and that in the urine after sodium sulphate the chlorides nearly disappear.

The first experiments were made with kidney substance and are similar to those which Loeb performed in connection with the osmotic pressure of muscle. The kidney cortex left in a 1.2—1.5 per cent. solution of sodium chloride for half-an-hour takes up water, but if the concentration is raised to 1.8 per cent. it loses water amounting to 1—2 per cent. of its weight. Liver and spleen behave very similarly. In the kidney medulla, the tissue takes up water from sodium chloride solutions of higher concentration; hence it is regarded as improbable that during life the epithelium will absorb water from a less concentrated urine.

If the two salts sodium chloride and sodium sulphate are administered to an animal simultaneously, they do not affect each other. The absolute amounts excreted are the same as when each is given alone. During the diuresis produced in an animal by one salt, the increased amount of urine caused by giving the second leads to a greater absolute

quantity of the second salt in the urine. This apparent contradiction probably depends on the specific water and salt exchange between blood, tissues, and lymph. In 'salt-poor' animals, diuresis caused by diuretin is accompanied by a rise in the sodium chloride of the urine. The same is true for various substances which cause diuresis by acting poisonously on the kidney substance; there is no such increase in salt concentration if water alone is employed. If the nerves of one kidney are cut, that kidney, when salt is given, secretes urine less in amount but of greater concentration than that secreted by the other. Removal of the kidney capsule produces the opposite effect. If both operations are performed, the effect of the removal of the capsule predominates.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Assimilation of Free Nitrogen by Bacteria. MARTINUS W. BEIJERINCK and A. VAN DELDEN (*Centr. Bakt. Par.*, II, 1902, 9, 3—43).—The absorption of gaseous nitrogen which occurs when garden soil is brought into culture media containing only traces of nitrogen compounds along with dextrose or mannitol and potassium phosphate, appears to be largely due to a symbiosis between *Azotobacter chroococcum* and certain species of *Granulobacter*, *Aerobacter aerogene*, or *Bacillus radiobacter*. Of these, the granulobacter species are able to take up free nitrogen by themselves, but none of the others can do this. In the presence of *Chroococcum*, however, absorption of nitrogen occurs in all three cases, although it has not been decided which organism actually assimilates the nitrogen. The amount of nitrogen taken up varies considerably in different cases, but is at its maximum when a mixture of bacteria obtained by sub-cultivation from garden earth is employed, and then amounts to about 7 mg. per gram of sugar or mannitol decomposed, or about 138 mg. per litre of culture medium. In mixtures containing *Granulobacter* and *Chroococcum*, the former of these takes up the nitrogen, producing a soluble compound which serves for the nutrition of the accompanying organism, and this develops extremely well under these conditions, forming a voluminous, slimy mass. The nitrogen contained in this is readily converted into nitrate when a little fresh soil is introduced, the conversion of atmospheric nitrogen to nitrate being thus completed. The nature of the soluble nitrogen product formed from gaseous nitrogen has not yet been ascertained, but it does not appear to be ammonia, a nitrite, or a salt of hydrazine or hydroxylamine.

A. H.

Organisms of Nitrification. W. OMELIANSKI (*Centr. Bakt. Par.*, II, 1902, 9, 63—65, 113—117).—The organism which converts nitrites into nitrates is not able to bring about the oxidation either

of sodium sulphite or sodium phosphite, even when a good growth occurs in the presence of these salts.

All attempts to detect the presence of an oxydase secreted by the organism which oxidises ammonia to nitrite, either in the filtered medium or in the disintegrated bacteria, proved quite unsuccessful.

A. H.

Nitrogen Assimilation and Proteid Formation of Moulds. FRIEDRICH CZAPEK (*Beitr. chem. Physiol. Path.*, 1902, 2, 557—590. Compare Abstr., 1902, ii, 280).—The present paper deals with the utilisation of amines, amides, and ammonium salts in the production of proteids in *Aspergillus niger*. As regards alkylamines, the results show that suitable sources of nitrogen are to be found among primary, secondary, and tertiary amines, whilst quaternary ammonium compounds are very injurious. The suitability of alkylamines as a source of nitrogen increases with the amount of carbon and the mol. weight. Isomeric compounds show marked differences, triethylamine being more suitable than dipropylamine. The presence of hydroxyl groups is favourable.

Acetamide and propionamide are good sources of nitrogen, whilst the other amides of the series are quite unsuitable. Lactamide is better than the corresponding propionamide. The amides of dibasic acids all gave good results. Nitriles are, on the whole, unsuitable as sources of nitrogen; amygdalin gave the best results. Amidines are, as might be expected, relatively good sources of nitrogen.

Urea and its derivatives are inferior, as sources of nitrogen, to amino-acids and alkylamines. Acid ureides gave good results, being presumably readily converted into amino-acids.

Ammonium salts of the acetic acid series are not, on the whole, suitable as sources of nitrogen for *Aspergillus niger*, whilst the salts of the oxalic acid series proved to be very suitable; good results were obtained with ammonium oxalate when carbon was supplied in the form of sugar.

N. H. J. M.

Denitrification. E. B. VOORHEES (*J. Amer. Chem. Soc.*, 1902, 24, 785—823. Compare Abstr., 1901, ii, 341).—The experiments were made in large cylinders with two kinds of soil, a medium clay and a sandy loam, each series comprising 60 cylinders. The two series included twenty different conditions of manuring. As regards denitrification, the result of laboratory experiments showed the destruction of nitrates in presence of organic matter, most of the loss being as free nitrogen.

The percentage recovery of nitrogen in crops from the different manures, when applied singly, was as follows: fresh solid manure, 19.78; fresh solid and liquid manure, 38.61; leached solid manure, 16.50; leached solid and liquid manure, 26.94; sodium nitrate, 5 grams per cylinder, 77.22, and 10 grams per cylinder, 75.03; ammonium sulphate, 65.84. When the manures were combined, there was, in six cases out of ten, a gain over the sum of the increase on the materials when used alone. No denitrification took place in these experiments. No residual effect was observed in the case of quick-

acting manures ; there may even be a diminished yield owing to a greater amount of soil nitrogen being used under the influence of the manure.
N. H. J. M.

Digestion of Amœbæ, and their Intracellular Diastase. HENRI MOUTON (*Ann. Inst. Pasteur*, 1902, 16, 457—509).—The paper contains a detailed account of the investigation of a definite species of amœba, which the author has isolated and grown. From it, he has isolated a ferment (diastase) which has a proteolytic action resembling that of trypsin.
K. J. P. O.

Utilisation of Mineral Principles by Grafted Plants. LUCIEN DANIEL and VICTOR THOMAS (*Compt. rend.*, 1902, 135, 509—512).—The results of experiments with beans showed that grafting diminished transpiration, and considerably affected the amount of mineral matter absorbed. At the same time, the phenomenon of chlorosis was greatly modified by grafting.
N. H. J. M.

Utilisation of Ternary Carbon by Plants and Microbes. PIÉRRÉ MAZÉ (*Ann. Inst. Pasteur*, 1902, 16, 433—451).—Experiments on the feeding of mycelium with the four food stuffs, sugar, alcohol, glycerol, and lactic acid, have shown that in all cases the elementary composition of the mycelium remains the same ; the food is oxidised to aldehyde, carbon dioxide, and water, the amount of the former varying with the nature of the food-stuff. The respiratory quotient seems to depend more on the state of the culture than on the nature of the food-stuff. *Eurotiopsis* ferments sugar with an energy comparable to that of yeast.
K. J. P. O.

Detection of Fatty Oil and its Formation, especially in Olives. C. HARTWICH and W. UHLMANN (*Arch. Pharm.*, 1902, 240, 471—480).—The microchemical reactions which serve for the detection of fatty oils are first dealt with, the method chiefly considered being that of saponifying the oil globules under the microscope with a strong solution of potassium hydroxide and ammonia and observing the crystals of soap which are formed (Molisch, 1901).

The oil of gentian root was examined and found to be a fat of the nature of cholesterol.

An investigation was made of the formation of the oil in the fruit of the olive, the fruit being examined during 1901 and 1902 at various stages of its development ; it was obtained from San Remo. The percentage of oil in the fruit was as follows : July 18, 0.55 ; Aug. 7 and 16, 5.02 ; Sept. 12, 16.3 ; Oct. 28, 21.3 ; Dec. 15, 22.7 ; Jan. 16, 22.85 ; Feb. 18, 20.8. It is from dextrose that the oil is formed.

C. F. B.

The Composition of the Reserve Carbohydrates of the Albumen of some Palms. E. LIÉNARD (*Compt. rend.*, 1902, 135, 593—595).—The carbohydrates in the grains of I, *Areca catechu* ; II, *Chamærops excelsa* ; III, *Astrocaryum vulgare* ; IV, *Cenocarpus*

bacaba ; V, *Erythea edulis* ; and VI, *Sagus Rumphii*, have been investigated. The results are summarised in the following table :

	I.	II.	III.	IV.	V.	VI.
Water	6.312	11.38	7.65	1.34	1.038	11.4
Fat	7.25	2.09	59.52	1.30	10.3	0.376
Initial reducing sugar	0.263	0	0	0	0.221	0
Sucrose	0.336	0.912	1.613	0.683	1.061	1.102
Reducing sugar (total obtained by successive hydrolysis, expressed as dextrose)	31.45	56	44.65	54.31	41.88	40.38
Reducing sugars:						
As mannose...	22.85	49	31.97	41.77	36	33.72
As galactose	0.687	0.73	0.758	1.007	1.005	0.646

J. McC.

Ash Constituents of Plants. Their Estimation and their Importance for Agricultural Chemistry and Agriculture. BERNHARD TOLLENS (*J. Landw.*, 1902, 50, 231—275).—The methods of determining total ash and ash constituents are discussed, as well as the various conditions which affect the composition of the ashes of plants, such as the period of growth, character of the soil, manuring, &c.

N. H. J. M.

Feeding Experiments with Fish Meal, Maize (Oil) Cakes, and Wheat Bran. J. KLEIN (*Milch. Zeit.*, 1902, 31, 369—372).—Systematic feeding of pigs showed that the maize meal was of the same food value as barley, wheat bran being somewhat inferior to the latter. With fish meal, the results were not so conclusive, as the animals at first showed repugnance to this food. Afterwards, it appeared to have a fair food value.

W. P. S.

Daily Variations in the Amount of Fat in Milk. M. SIEGFELD (*Bied. Centr.*, 1902, 31, 716 ; from *Landw. Centr. Prov. Posen*, 1902, 58).—Fat was determined each day, for a year, in the milk of ten dairies. The most frequent variations in the amounts of fat in two successive days were from 0.1 to 0.3 per cent. Differences of more than 0.5 per cent. in two successive days occurred in most cases, and are not uncommon when the yield of milk is under 50,000 litres.

N. H. J. M.

Yellow Lupins. PIERRE P. DEHÉRAIN and E. DEMOUSSY (*Compt. rend.*, 1902, 135, 445—449).—Yellow lupins can be grown on strong soils as well as on sandy soils. In neutral soils, they can be grown in presence of small amounts of calcium carbonate, but not in peaty soil to which calcium carbonate has been applied. In any case, the ash of yellow lupins always contains much calcium carbonate.

The plants lived and ripened in soil containing 4 per cent. of

calcium carbonate, but did not, under these conditions, develop well, and the roots were free from nodules. The best growth is obtained in absence of calcium carbonate when a suitable variety of nodule bacteria is present. Bacteria which are suitable for white and blue lupins are not necessarily of use in the case of yellow lupins.

N. H. J. M.

Presence of Lime as Dolomite in certain Cultivated Soils. THOMAS L. PHIPSON (*Chem. News*, 1902, 86, 148).—Calcium and magnesium were determined in three Argentina cane soils which had been cultivated for several years, and in samples of the same soils, but uncultivated. It was found that the calcium was present as dolomite, and that the relations of calcium to magnesium remained essentially the same in the cultivated soils. The soils contained 70 to 84 per cent. of insoluble matter (sand, mica, and a little clay), about 0.8 per cent. of phosphoric acid, and about 0.12 per cent. of alkalis.

N. H. J. M.

Action of the Solid Constituents of Farmyard Manure. MAX GERLACH (*Bied. Centr.*, 1902, 31, 663—665; from *Jahresber. Landw. Versuchs-stat. Posen*, 1900—1901).—Oats and carrots were grown in pots containing 7 kilos. of loamy, sandy soil, manured, in addition to minerals, with sodium nitrate, farmyard manure, and extracted farmyard manure respectively. Whilst farmyard manure and, in a greater degree, sodium nitrate increased the yield of oats and carrots, extracted farmyard manure reduced the yield. Sodium nitrate alone gave better results than when applied along with extracted farmyard manure.

N. H. J. M.

Manurial Experiments with Kainite and "Forty per Cent. Potassium Salt." BACHMANN (*Bied. Centr.*, 1902, 31, 713—714; from *Fühling's Landw. Zeit.*, 1902, 147).—In experiments with winter rye on soil deficient in potash, "40 per cent. potassium salt" gave greater yields of grain and straw than kainite, and the simultaneous application of calcium hydroxide increased the yield more with "40 per cent. potassium salt" than with kainite. In the case of summer rye, kainite gave the better results, whilst with oats the results obtained were conflicting. "Forty per cent. potassium salt" gave better results than kainite with potatoes and (in seven out of eight experiments) mangels.

N. H. J. M.

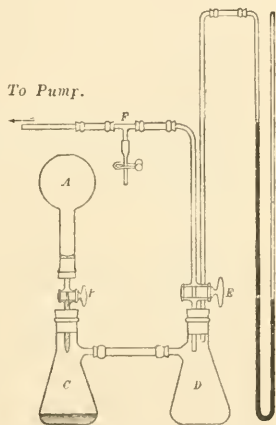
Reversion of Superphosphate of Lime in the Soil. WALTER F. SUTHERST (*Chem. News*, 1902, 68, 170—171).—The results of experiments on the action of calcium carbonate, magnesium carbonate, and limonite in rendering the phosphoric acid of superphosphate insoluble in water, showed that magnesium carbonate was the most, and calcium carbonate the least, active. Further experiments in which superphosphate was added, as well as mixtures containing limonite and varying amounts of calcium and magnesium carbonate, to clay soil showed that after 12 days 49.4 to 54.0 per cent. of the phosphoric acid was soluble in 1 per cent. citric acid solution.

N. H. J. M.

Analytical Chemistry.

Gas Analyses in Flasks. I. Estimation of the Quantity of Gas by the Measurement of a Certain Volume of Liquid. ALFRED WOHL (*Ber.*, 1902, 35, 3485—3492).—A gas is shaken up with liquid reagents in a stoppered flask and the solution is allowed to flow in until the residual gas is again under the ordinary pressure. The volume of liquid thus introduced is determined either by direct measurement or by weighing the flask before and after the experiment; this volume is equal to that of the gas absorbed. The paper contains sketches of a simple form of apparatus employed in filling the flask with the gas under examination. G. T. M.

Gas Analysis in Flasks. II. Estimation of the Amount of Gas by Determinations of the Pressure. ALFRED WOHL (*Ber.*, 1902, 35, 3493—3505).—A round-bottomed flask, *A*, is filled with the gas under slightly reduced pressure, and the liquid absorbent is introduced through the tap *B*. After the reaction is over, the flask is fitted into the Erlenmeyer flask, *C*, and the liquid withdrawn by placing the series of vessels in connection with the water-pump. When the residual gas again occupies the total volume of the flask *A*, its pressure is measured by means of the mercury manometer, and this adjustment is made after each absorption. The amount of gas left in the flask after any of these experiments is thus ascertained, because it is directly proportional to the pressure exerted. A slight transverse scratch is made at each of the opposite ends of the holes of the taps *E* and *B*, so that each tap has two of these pointing in opposite directions round its circumference. By means of this device, the taps can be opened or closed very gradually, and the action of the pump is thereby regulated so that the volume of the gas in *A* is readily adjusted. G. T. M.



The Degree of Accuracy of Iodometric Estimations. JOHANN PINNOW (*Zeit. anal. Chem.*, 1902, 41, 485—488).—The sensitiveness of the iodine starch reaction is largely influenced by the other substances in the solution (compare Meineke, *Abstr.*, 1895, i, 79). Eckstädt has stated (*Abstr.*, 1902, ii, 130) that the blue colour is not developed at greater dilutions than 0.000025 *N*, and Meineke found that 100 c.c. of dilute starch solution required 0.13 c.c. of *N*/100 iodine solution to produce the blue colour. The sensitiveness of the reaction is not

appreciably increased by increasing the amount of starch or by the addition of non-electrolytes, but is augmented ten-fold by adding electrolytes, the most active being sodium sulphate. When this salt is present in quantity corresponding with a 0.22 *N* solution, the blue colour is produced when the strength of the iodine solution exceeds 10^{-5} . 0.17 *N*.

M. J. S.

Detection of Fluorine in Beer and Wine. KARL WINDISCH (*Bied. Centr.*, 1902, 31, 720; from *D. Bierbrauer*, 1901, 49).—The fluorine is precipitated with ammonium carbonate and calcium chloride, separated by filtration, and ignited (without the filter). In this manner, less than 1 per million of fluorine in beer or wine can be detected.

N. H. J. M.

Estimation of Sulphur in Coal. CHARLES W. STODDART (*J. Amer. Chem. Soc.*, 1902, 24, 852—864).—0.5 Gram of the sample is burnt in an Atwater-Blakeslee bomb filled with compressed oxygen, the coal, which has been forced into a pellet, being fired by electricity. The gas is absorbed in a U-tube containing bromine water to oxidise any sulphur dioxide and after rinsing the bomb with water the filtrate which contains the bulk of the sulphuric acid is then treated as usual with barium chloride. The insoluble matter is also examined for sulphuric acid after a preliminary fusion with sodium potassium carbonate. The process is free from sources of error.

If the apparatus is not at disposal, the results nearest to the truth are those obtained by using Eschka's process (ignition with sodium carbonate and magnesium oxide). Before precipitating the sulphuric acid, it is advisable to separate any silicic acid. Several other published processes have been tried but were found to be more troublesome than Eschka's method.

L. DE K.

Detection of Hydrogen Sulphide. DOMENICO GANASSINI (*Chem. Centr.*, 1902, ii, 476—477; from *Boll. Chim. Farm.*, 41, 417—419).—A solution of 1.25 grams of ammonium molybdate in 50 c.c. of water is mixed with a solution of 2.5 grams of potassium thiocyanate in 45 c.c. of water, and to the mixture are added 5 c.c. of hydrochloric acid. The reagent will keep for a few days when placed in the dark. A strip of filter paper or a porcelain slab moistened with the reagent when exposed to vapours containing hydrogen sulphide will turn red. When testing mineral waters, the process may be applied as follows: 20 c.c. are mixed with 1—2 c.c. of a 20 per cent. solution of potassium thiocyanate, the liquid is acidified with dilute sulphuric acid and a few drops of a 5 per cent. solution of ammonium molybdate are added. In the presence of hydrogen sulphide, the liquid turns violet or red. In the presence of iron, it is as well to add a little oxalic acid. In the absence of hydrogen sulphide, the liquid turns yellow, but this colour disappears on agitating with ether, whilst the red colour is permanent.

L. DE K.

Iodometry of Sulphurous Acid. ERWIN RUPP (*Ber.*, 1902, 35, 3694—3695).—Sulphurous acid, after treatment with sodium car-

bonate, can be estimated by iodine if an excess of the latter is used and allowed to react for fifteen minutes before titration with thio-sulphate.
R. H. P.

Estimation of Tellurium. GUSTAV FRERICHS (*J. pr. Chem.*, 1902, [ii], 66, 261—262).—Telluric acid is instantly reduced by sulphur dioxide in presence of small quantities of potassium iodide. The reaction takes place less easily in presence of hydrobromic acid, and only very slowly in presence of an excess of hydrochloric acid. Telluric acid cannot be reduced by hydriodic acid alone (compare Peirce, *Abstr.*, 1896, ii, 673).
G. Y.

Iodometry of Phosphorous Acid and Phosphorus Trihaloids. ERWIN RUPP and A. FINCK (*Ber.*, 1902, 35, 3691—3693).—Phosphites can be estimated iodometrically provided the reaction is carried out in alkaline solution (sodium hydrogen carbonate is recommended) and that an excess of iodine is allowed to remain with the phosphite for at least two hours. The phosphorus trihaloids can be estimated in a similar manner after treatment with water.
R. H. P.

Rapid Volumetric Method for Estimating Phosphoric Acid in Fertilisers. A. L. EMERY (*J. Amer. Chem. Soc.*, 1902, 24, 895—897).—A slight modification of the volumetric method as published by the American Association of Official Agricultural Chemists, the most important change consisting in shaking the solution after precipitating with molybdic solution.
L. DE K.

Detection of Arsenic and Selenium in Sulphur. FRED. W. STEEL (*Chem. News*, 1902, 86, 135).—Two hundred grams of the sulphur are thoroughly extracted with carbon disulphide. The insoluble residue is treated with nitric acid, evaporated to dryness, dissolved in a little hydrochloric acid and water, and filtered. Twenty c.c. of hydrochloric acid, 1 c.c. of fairly concentrated stannous chloride solution, and 5 c.c. of sulphuric acid are added to the filtrate, the mixture being then warmed gently and left for some hours. If arsenic, or selenium insoluble in carbon disulphide, be present, a dark brown precipitate forms, which is collected on a small asbestos filter, washed, and dried at 100°. On heating the asbestos in a drawn-out tube, arsenic and selenium are volatilised into the narrow part of the tube, and by reheating the part of the tube containing the sublimate in a second tube, characteristic crystals of arsenious oxide and selenium dioxide are obtained. The latter may also be recognised by the odour at the open end of the tube. In the entire absence of water, selenium dioxide forms fern-shaped crystals, but as traces of water are almost always present, minute globules are found in place of crystals. Should no selenium be found associated with the arsenic, the carbon disulphide solution must be evaporated, the sulphur treated with a large volume of nitric acid, and the process proceeded with as above.
W. P. S.

Apparatus for the Detection and Estimation of Minute Traces of Arsenic. EDWIN DOWZARD (*Chem. News*, 1902, 86, 3).—The apparatus consists of a test-tube on a foot and having at the

top a scrubbing chamber filled with beads. Above this, and fitting into it, is a tube which is broadened out at its upper end so as to form a small table, the orifice in the centre being 3 mm. in diameter. Hydrogen is generated in the test-tube and a piece of filter-paper, moistened with a drop of mercuric chloride and dried, is secured over the orifice. By preparing a standard set of arsenical stained papers, the process may be applied quantitatively.

W. P. S.

Reaction between Potassium Iodide and Mercuric Chloride and its Analytical Application. LUCIEN L. DE KONINCK and J. LEBRUN (*Chem. Centr.*, 1902, ii, 72—73; from *Bull. Assoc. Belg. Chim.*, 16, 127—139).—This reaction was first applied by Marozean in 1832 for the estimation of potassium iodide by titration with mercuric chloride solution. When all the potassium iodide has been converted into the salt $2KI, HgI_2$, further addition of mercuric chloride causes a turbidity (HgI_2) to appear; this indicates that the titration is completed. Lebrun has found that the method does not give accurate results, being influenced by temperature, dilution, and the presence of other salts. It, however, is accurate, provided that cyanides and bromides are absent and that the titration is made at a temperature between 15° and 20° . Approximately, *N*-potassium iodide gave the best results when titrated with *N*/2 mercuric chloride. The titre of the latter should be determined under conditions identical with those in which the estimations are carried out.

W. P. S.

Iodometry of the Peroxides of Calcium, Strontium, Barium, Magnesium, and Sodium. ERWIN RUPP (*Arch. Pharm.*, 1902, 240, 437—449. Compare *Abstr.*, 1900, ii, 572).—The available oxygen in all these substances but the last can be determined by mixing 0.15—0.2 gram of the substance with 1 gram of potassium iodide, 30 c.c. of water, and 5 c.c. of 25 per cent. hydrochloric acid in a stoppered bottle, allowing the mixture to remain in the dark for half-an-hour (1 hour in the case of magnesium peroxide), and then titrating the liberated iodine with *N*/10 thiosulphate solution. The accuracy of the method was controlled by comparison with other methods, namely, titration of the peroxide with potassium permanganate or with an arsenite solution. Of the purchased samples examined, the calcium peroxide appeared to be 101.5, hydrated barium peroxide 96.5, anhydrous barium peroxide 92.5, strontium peroxide 51.5, and magnesium peroxide 3 per cent pure.

In the case of sodium peroxide, the following modification of the method is necessary. To 0.1—0.2 gram of finely powdered substance, there is added rapidly in one operation 25 c.c. of saturated baryta water; after 10 minutes, the liquid and precipitate are rinsed into a solution of 1—2 grams of potassium iodide and 5 c.c. of 25 per cent. hydrochloric acid in about 30 c.c. of water, shaken until a clear solution is obtained, covered, allowed to remain for half-an-hour, and then titrated with thiosulphate. Even with these precautions, the available oxygen found is less than that evolved on treatment with cobalt nitrate solution (*Archbutt, Abstr.*, 1895, ii, 186). This is supposed to be due

to the presence of peroxides richer in oxygen than Na_2O_2 , which, however, give off the extra oxygen when they react with barium hydroxide.

C. F. B.

Cement Analysis. W. HARRY STANGER and BERTRAM BLOUNT (*J. Soc. Chem. Ind.*, 1902, 21, 1216—1223).—The following methods are given :

1. *For Silica and Chief Bases*, 0.5 gram of the cement is mixed in a china basin with a few c.c. of water, 20 c.c. of hydrochloric acid of sp. gr. 1.15 are added and allowed to act for a few minutes. No silica is precipitated. The contents of the basin are then evaporated to dryness and baked at a temperature of 200° for an hour. The residue obtained is digested with 30 c.c. of hydrochloric acid of sp. gr. 1.15, and the silica, together with the insoluble residue, filtered off. Repeated evaporations of the filtrate are unnecessary (compare Abstr., 1902, ii, 427). The filtrate is returned to the basin, excess of ammonia is added, and heat applied until nearly all excess of ammonia is driven off. After removing the aluminium and ferric hydroxides by filtration, the lime is precipitated in the filtrate as usual with ammonium oxalate. The filtrate from the latter is evaporated to a pasty mass, 40 to 50 c.c. of nitric acid of sp. gr. 1.4 are added, and the heating is continued until the ammonium salts have been volatilised. The residue is dissolved in a few c.c. of water, 6 drops of hydrochloric acid and excess of ammonia are added, and then 2 drops of ammonium oxalate solution (4 per cent.). A small precipitate, consisting of silica, aluminium and ferric hydroxides, and calcium oxalate, is obtained and removed by filtration. This silica is derived from the glass vessels used, and may be ignored, whilst the remainder of the precipitate belongs to the cement. In very exact work, the constituents must be separated and weighed. The magnesia in the filtrate is estimated as pyrophosphate as usual.

2. *For Insoluble Residue and Sulphur Trioxide*, 0.5 gram of the cement is evaporated with hydrochloric acid, as just described, but not baked. After filtration, the precipitate is digested with a saturated solution of sodium carbonate, which leaves the inert acid silicates undissolved. The filtrate from the silica is precipitated with barium chloride to obtain the sulphur trioxide.

3. *For Loss on Ignition*.—0.5 gram is heated in a muffle-furnace at a temperature below the maximum obtainable. Ignition over a blast flame causes loss of sulphur trioxide.

4. *For Carbonates*.—Gravimetric estimation of the carbon dioxide.

5. *The Alkalis* are weighed as chlorides and separated by the use of platinic chloride, after removing the silica and chief bases in the cement, volatilising the ammonium salts, and separating the magnesia with barium hydroxide, excess of the latter being precipitated with ammonium carbonate.

6. *The Alumina and Ferric Oxide* are separated by the sodium hydroxide process.

Second precipitations of the precipitates obtained by the above methods are not necessary.

In the case of cement raw material an analysis of the mixture when

ready for burning may be made as previously described, after first heating the portion to be analysed over the blast flame. W. P. S.

Cement Analysis. R. F. YOUNG and B. F. BAKER (*Chem. News*, 1902, 86, 148).—For the estimation of calcium oxide in cement, 1 gram of the latter is treated with a small quantity of concentrated hydrochloric acid, a little nitric acid is added, and the whole evaporated to dryness. After heating the residue until it is distinctly red, dilute hydrochloric acid is added and then excess of ammonia. The silica, ferric hydroxide, and aluminium hydroxide are separated by filtration and the lime is precipitated in the filtrate as usual with ammonium oxalate. Should it be preferred to treat the cement originally with dilute hydrochloric acid, the precipitate produced by ammonia must be redissolved in concentrated hydrochloric acid and reprecipitated with ammonia. In both methods, it is advisable to estimate the traces of silica, alumina, and iron which remain in the calcium oxide obtained. Simple treatment of the cement with dilute hydrochloric acid was not found to decompose the whole of the calcium silicate. The volumetric method (titration of the excess of a known volume of oxalic acid left after precipitating in ammoniacal solution) gave low results.

W. P. S.

Analysis of Lithopone. CH. COFFIGNIER (*Bull. Soc. chim.*, 1902, 27, [iii], 943—947. Compare Abstr., 1902, ii, 630).—The low figures obtained in the analysis of some samples of lithopone are due to the presence therein of zinc hydroxysulphide owing to insufficient calcination of the crude precipitate.

T. A. H.

Clinical Method for Estimating Mercury in Urine. SCHUMACHER (II) and W. JUNG (*Zeit. anal. Chem.*, 1902, 41, 461—484).—If more than 0.6 mg. of mercury per litre is present, 500 c.c. of the urine will suffice; otherwise, a larger volume should be concentrated, some sodium chloride being added to prevent volatilisation of mercuric chloride. Fifty c.c. of concentrated hydrochloric acid and 5 grams of potassium chlorate are added, and the mixture boiled. After cooling to 80°, 12 grams of chemically pure rasped zinc are added, and later 3 grams more. In about 2 hours, every trace of mercury will have united with the undissolved zinc. The upper liquid is decanted; the zinc is washed, treated with dilute potassium hydroxide, and again washed. It is then dissolved in 50 c.c. of dilute hydrochloric acid, with addition of chlorate. After boiling out most of the chlorine, the last traces are removed by adding alcohol. Hydrogen sulphide solution is added, the mixture is made up to 100 c.c., and the yellowish-brown colour is compared colorimetrically with standards which are either freshly prepared from mercuric chloride, or may consist of suitable mixtures of dyes. Mixtures of the Janus black, brown, and yellow of Meister, Lucius, and Brüning have successfully imitated every shade and intensity of mercuric sulphide coloration. A gravimetric method is also described in which the mercury is collected in a filter of gilt asbestos and the amount ascertained from the loss of weight on ignition.

M. J. S.

Estimation of Cerium Dioxide and of Didymium Oxide by Iodine. RICHARD JOS. MEYER and M. KOSS (*Ber.*, 1902, 35, 3740—3746. Compare *Marc, Abstr.*, 1902, ii, 503).—Cerium dioxide may readily be estimated by boiling with hydrochloric acid and potassium iodide. It is necessary to take only a slight excess of iodide and to heat the mixture gradually. It is shown that prolonged ignition of the dioxide does not produce slight reduction, as generally stated. Small amounts of didymium oxide (Di_2O_3) interfere with the estimation of cerium dioxide; in all cases, more than the theoretical amount of iodine is liberated.

When praseodymium peroxide (Pr_2O_5) is reduced to the lower oxide (Pr_2O_3) in a stream of hydrogen, the loss in weight corresponds with the reduction of only 64.4 per cent. of the higher oxide. Similar results are obtained when the lower oxide is oxidised by ignition in an atmosphere of oxygen, and also when the dioxide is estimated by iodine. Pure neodymium oxide does not lose in weight when heated in a current of hydrogen, and does not liberate iodine.

In the presence of considerable amounts of cerium dioxide, it appears that the whole of the praseodymium oxide, and not merely 66.4 per cent., can liberate iodine.

Mixtures of praseodymium and neodymium oxides vary in colour and activity according to the relative amounts present. Mixtures containing small amounts of praseodymium are colourless and inactive; those containing relatively large amounts appear brown, and the activity agrees with the amount of praseodymium present.

J. J. S.

Photometric Estimation of Iron. J. T. D. HINDS and MYRTIS LOUISE CULLUM (*J. Amer. Chem. Soc.*, 1902, 24, 848—852).—The authors have successfully used Hinds's photometric method (*Abstr.*, 1896, ii, 574) for the estimation of ferric iron. As, however, ferric ferrocyanide is slightly soluble in excess of either ferric chloride or potassium ferrocyanide, the estimation must be made as follows: the solution is placed in a beaker in quantity sufficient to fill the photometer and a 5 per cent. solution of potassium ferrocyanide is added from a burette until the photometer readings, which at first gradually decrease, begin to show an increase again. The lowest reading is the one adopted.

The process is mathematically explained and a table is given showing the percentage of iron corresponding with the number of c.c. of ferrocyanide used.

L. DE K.

Iron Analysis. GEORGE T. DOUGHERTY (*Chem. News*, 1902, 86, 28—30; from *The Iron Age*, 1902, May 8).—*Complete Evolution Method for the Estimation of Sulphur in Iron.*—Five grams of drillings are strongly heated in a covered china crucible, a layer of filter paper being placed over the drillings before commencing the ignition. The latter is completed in 15 minutes, when the contents of the crucible are transferred to the evolution flask and the liberated hydrogen sulphide absorbed in potassium hydroxide solution, which is afterwards acidified and titrated with standard iodine as usual.

Estimation of Graphite by Direct Weighing.—One gram of drillings is gently heated with 60 c.c. of nitric acid of sp. gr. 1.13 for 30 minutes and then boiled for 5 minutes. The insoluble residue is collected in a weighed Gooch crucible containing a disc of filter-paper and washed once with dilute nitric acid, three times with hot water, twice with hot 10 per cent. potassium hydroxide solution, twice with hot dilute hydrochloric acid, then with hot water, alcohol, and ether, and dried at 120°. The weighed residue, consisting of graphite and silica, is ignited and the weight of the latter obtained.

Continual Diminution of Graphite in much used Drillings.—Attention is drawn to the mechanical loss of graphite by samples which have been often mixed or turned over, or even on powdering and sifting.

Estimation of Manganese in Iron and Steel.—One gram of the sample is heated with 20 c.c. of nitric acid of sp. gr. 1.13, evaporated, diluted, precipitated with emulsion of zinc oxide, and made up to 300 c.c. The whole is then poured into a beaker, allowed to settle, and 150 c.c. of the supernatant liquid boiled and titrated with standard permanganate solution, the titre of the latter being obtained on a sample of iron containing a known quantity of manganese.

W. P. S.

Estimation of Iron in Urine. GOSWIN ZICKGRAF (*Zeit. anal. Chem.*, 1902, 41, 488—494).—Diluted egg-albumin is added to the urine and coagulated by heat after acidifying with acetic acid. The coagulum is collected, dried, and incinerated, and the ash is fused with potassium hydrogen sulphate, reduced with zinc, and then titrated. A correction is required for the iron in the white of egg.

M. J. S.

Estimation of Alcohol in Dilute Solutions. G. ARGENSON (*Bull. Soc. chim.*, 1902, 27, [iii], 1000—1003).—The following materials are required, a saturated solution of potassium dichromate and a 0.05 per cent. solution of magenta decolorised to a faint pink tint by means of sulphur dioxide. The estimation is carried out by adding to 20 c.c. of the liquid containing from 1/200000 to 1/100000 of its volume of alcohol, 5 c.c. of the dichromate solution and 1 c.c. of sulphuric acid. This mixture is then distilled, and the first 5 c.c. collected in a test-glass containing a like quantity of the decolorised magenta solution. The tint so produced is then matched by means of a potassium permanganate solution previously standardised against the distillate from a liquid containing a known amount of alcohol.

T. A. H.

Estimation of Pentoses and Pentosans. BERNHARD TOLLENS (*Zeit. physiol. Chem.*, 1902, 36, 239—243).—Attention is again drawn to the investigations of Kröber and Rimbach (compare Abstr., 1902, ii, 537—538), and Kröber's tables are given for calculating furfuraldehyde, arabinose, araban, xylose, xylan, pentose, and pentosan from the amount of phloroglucide found, in milligram differences from 0.030

gram to 0.300 gram. The author thinks that Grund (Abstr., 1902, ii, 415) was not aware of Kröber and Rimbach's work on this subject.

W. P. S.

Colorimetric Process for the Detection of Very Small Quantities of Sugar. VENTRE (*Zeit. Ver. deut. Zuckerind.*, 1902, 560, 788—789).—The process involves the use of (1) pure sulphuric acid, (2) a solution of nitrobenzene in an equal volume of alcohol, and (3) a saturated solution of pure ammonium molybdate. To 10 c.c. of the solution, previously clarified with lead acetate, filtered, and placed in a large test-tube, 12 drops of the sulphuric acid, 5 of solution (2), and 20 of (3) are slowly added, the liquid being then kept boiling for three minutes over a spirit flame. The solution is then poured into a small test-tube and left for some time, when a blue coloration appears, the intensity of which is compared with that given by liquids containing known amounts of sugar. The method is very sensitive and admits of the detection of 0.000001 per cent. of sugar. It can be used for testing diabetic urine or, combined with the measurement of the polarisation, for determining the amounts of sucrose, dextrose, and lævulose in sugar-cane juices.

T. H. P.

Estimation of Glycogen. ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1902, 36, 257—260).—The Pflüger-Nerking method for the estimation of glycogen in livers being tedious and liable to give inaccurate results, the following method is suggested. The fresh liver is minced, extracted with absolute alcohol, then with ether, and powdered. From 5 to 10 grams of the powder are treated with potassium hydroxide solution (2 to 3 per cent.) and allowed to settle. An aliquot part of the clear, supernatant liquid is then precipitated by the addition of twice its volume of alcohol. The precipitate is washed first with 60 per cent. alcohol and then with absolute alcohol. The resulting product, after drying for 8 hours at 105°, consists of glycogen, free from nitrogen, but containing some mineral matter, which is separately estimated. By digesting the powdered liver in artificial gastric juice, afterwards neutralising the solution, filtering, and treating the evaporated filtrate with alcohol, the glycogen is also obtained containing only traces of nitrogen and a little mineral matter. A small amount of glycogen is retained in the coagulum formed on neutralising the digestive solution.

W. P. S.

Halphen's Test for Cotton Seed Oil. B. SJOLLEMA and J. E. TULLEKEN (*Zeit. Nahr. Genussm.*, 1902, 5, 914—916).—The coloration obtained when Halphen's test is applied to butters from cows which have been fed on cotton seed meal, is identical with that given by cotton seed oil itself. On spectroscopically examining the colour produced in the oil, it was found that by heating at a temperature of 55°, an absorption band appeared in the yellow part of the spectrum having its maximum at $\lambda 550$; a thicker layer gave a maximum more to the left at $\lambda 570$. By long heating, or by employing a higher temperature (110°), a second band was noticed at $\lambda 490$, but a thick layer could not be examined, owing to the darkening of the right half of the spectrum.

After considerable dilution with amyl alcohol, the maximum of this second band was distinct at $\lambda 490$, whilst the band in the yellow had lost much of its intensity.

W. P. S.

Estimation of Urea by Folin's Method. By CARL ARNOLD and CURT MENTZEL (*Zeit. physiol. Chem.*, 1902, **36**, 49—52).—The writers find, as the result of their experiments, that this process (Abstr., 1901, ii, 630) does not yield the whole of the ammonia produced by the decomposition of the urea in urine. The amount of ammonia obtained from uric acid, hippuric acid, creatine, &c., was also below the theoretical quantity.

W. P. S.

Estimation of Xanthine Bases and Uric Acid in Urine. By G. GITTELMACHER-WILENKO (*Zeit. physiol. Chem.*, 1902, **36**, 20—27).—The method described by Niemilowicz (Abstr., 1902, ii, 542) was found to be as accurate as that of Salkowski. A combination of the methods of Niemilowicz and Denigès (Abstr., 1894, ii, 403) for the estimation of uric acid in urine gave accurate results. The purine derivatives (total) were estimated by Denigès's method, and the xanthine bases by that of Niemilowicz. The difference between the number of c.c. of 50/*N* silver solution used in the two methods, multiplied by 4.2, gives milligrams of uric acid in 100 c.c. of urine.

W. P. S.

Estimation of Albumin. By ADOLF JOLLES (*Monatsh.*, 1902, **23**, 589—598. Compare Abstr., 1901, ii, 688).—The albumin of urine is coagulated in dilute acetic acid solution, washed free from chlorine, and oxidised by potassium permanganate in dilute acid solution. When thus treated, the albumin yields products which, on addition of sodium hypobromite, evolve a fixed proportion of the total nitrogen. The weight of the nitrogen evolved is multiplied by 7.68 to find the weight of the albumin. It is claimed that the method is simpler and more free from sources of error than the methods usually adopted for the estimation of albumin.

G. Y.

Detection of Saccharin in Milk. By CARLO FORMENTI (*Chem. Centr.*, 1902, ii, 541—542; from *Boll. Chim. Farm.*, **41**, 453—458).—One hundred c.c. of the sample are mixed with 1 c.c. of acetic acid of sp. gr. 1.038 and heated for half-an-hour on a water-bath. The filtrate and washings are shaken in a separating funnel with 50 c.c. of a mixture of ether and light petroleum after adding 5 c.c. of sulphuric acid of sp. gr. 1.134; towards the end, a little alcohol is also added. The residue obtained by evaporating the ethereal solution is then tested for saccharin as usual, the most characteristic proof being afforded by the taste.

L. DE K.

General and Physical Chemistry.

Effect of Mercury Vapour on the Spectrum of Helium. J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1902, 71, 25—27. Compare Ramsay and Collie, *Abstr.*, 1896, ii, 633).—The helium spectrum, as observed in a Plücker tube, consists of eight lines, and even in the presence of mercury the full spectrum is observed in the capillary portion of the tube. The presence of mercury, however, has an effect in other ways, causing the disappearance at the negative electrode of a red, a blue, and a violet line (the yellow line becoming faint), whilst in the wider central portion only one green line is visible. The lines which persist and those which disappear in the negative glow after the admission of mercury correspond with the two systems referred to by Runge and Paschen (*Abstr.*, 1896, ii, 1), and the differentiating effect of mercury on the helium spectrum might be taken as evidence in favour of their view that helium is a mixed gas, were it not that the spectra of argon, neon, and krypton are also altered by mercury vapour.

The author recommends a helium-mercury tube containing a trace of hydrogen as a standard in spectroscopic measurements. J. C. P.

Orienting Action of Light on the Sublimate Produced in Sunlight. P. N. RAIKOW (*Chem. Zeit.*, 1902, 26, 1030—1032).—A series of remarkable experiments on the sublimation of benzoic acid, iodine, naphthalene, and camphor in sunlight are described. In a closed desiccator, illuminated on one side by the sun, it was found that sublimation took place with great rapidity, the sublimate being deposited only on the illuminated side. Thus it was found that 1 gram of iodine placed on the bottom of a desiccator was in a few days completely transferred to the upper half of the desiccator and deposited only on the illuminated side. Then, on turning the desiccator round so that the other side was illuminated, it was found, especially in the case of camphor, that the sublimate passed over to the sunny side again. In the case of coloured substances, such as iodine, increase of the intensity of the light is accompanied by an increase of the rate of sublimation. K. J. P. O.

Sensitiveness to Light of Colourless Organic Compounds. JOHANNES PINNOW (*J. pr. Chem.*, 1902, [ii], 66, 265—320. Compare *Abstr.*, 1901, ii, 368).—The diminution of fluorescence, referred to in the author's previous paper, is due to absorption of light by the colourless compound. If the effect is obtained with a screen of the colourless solution, decomposition of the colourless substance by the action of light is diminished by a screen of the fluorescent solution. If the diminution of fluorescence is observed only with a mixture of the solutions, the fluorescent substance acts as a sensitiser towards the colourless compound and facilitates its decomposition by light. A quantitative expression of the effect cannot be obtained. The property of

diminishing fluorescence is characteristic of certain molecular configurations. A group which increases the diminution of fluorescence increases the absorption of light by the molecule in which it occurs, and therefore favours its decomposition by light. Conversely, the presence of a group which is found to lessen the diminution of fluorescence increases the stability of a dye towards light. G. Y.

Constancy of Time characteristic of the Disappearance of Radioactivity induced by Radium in a Closed Space. P. CURIE (*Compt. rend.*, 1902, 135, 857—859. Compare Abstr., 1901, ii, 216, 298; 1902, ii, 58).—The rate at which induced radioactivity decreases has been investigated both in the case of solid material freely exposed to the air or enclosed (either in a gas, air, hydrogen, or carbon dioxide, or in a vacuum), and also in the case of the walls of the vessel which has formed part of the boundaries of the space enclosing the radioactive material. The rate of decrease in all cases follows an exponential law, $I = I_0 e^{-t/\theta}$, where I is the intensity after time t , I_0 the initial intensity, e the base of the Napierian logarithms, and θ a constant representing time; the value of θ is 4.97×10^{-5} seconds (or 5.752 days). The value of this constant is not affected by the use of different salts of radium, either in solution or in the solid state, by the size or form of the enclosed space, by the nature of the glass, by using enclosures of copper or aluminium instead of glass, by varying the form of the communicating tubes between the radium compound and the space in which radioactivity is to be induced, by varying the time of exposure to the radium from 15 minutes to one month, by working under a high pressure or in a vacuum, and by replacing air by hydrogen or carbon dioxide.

The rate of decrease was measured by placing the tube in which radioactivity has been induced in a cylinder of aluminium, which is then placed between the armatures of a condenser. A P.D. of 450 volts is maintained between these armatures. The air between the armatures is rendered conducting by the radiations, and the resulting current measured. K. J. P. O.

Chemical Action of the Canal Rays. GERHARD C. SCHMIDT (*Ann. Physik.*, 1902, [iv], 9, 703—711. Compare Abstr., 1902, ii, 237).—According to Wien's investigations, the canal rays carry a positive charge, and it was thought that they might exhibit an oxidising effect, in contrast to the negatively charged cathode rays, which were recently shown by the author (*loc. cit.*) to have a strong reducing action. The chief chemical effect of the canal rays, however, seems to be decomposition, and the intensity of the luminescence induced in certain solid solutions by the canal rays diminishes very rapidly on that account. When a tube containing oxygen and an oxidisable substance (such as copper or zinc) is exposed to the action of the canal rays, oxidation takes place, probably through the agency of oxygen atoms produced by decomposition of the oxygen molecules. Similarly, when a tube containing hydrogen and a reducible substance is exposed to the action of the canal rays, reduction takes place.

The most characteristic effect of the canal rays is the decomposition of sodium salts, discovered by Arnold (*Ann. Physik.*, 1897, 61, 326).
J. C. P.

Electro-affinity Theory of Abegg and Bodländer. JAMES LOCKE (*Amer. Chem. J.*, 1902, 28, 403—410).—A reply to Abegg and Bodländer (Abstr., 1902, ii, 642).
E. G.

Researches on Voltaic Elements Depending on the Reciprocal Action of Two Saline Solutions. MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 27, 145—271).—This communication includes six memoirs containing a detailed account of work already published (compare Abstr., 1902, ii, 375, 376, 439, 440, 546, 591).
G. T. M.

The Dissociation Constant of Water and the Electromotive Force of the Gas Element. G. PREUNER (*Zeit. physikal. Chem.*, 1902, 42, 50—58).—In the reactions represented by $2\text{CO} + \text{O}_2 = 2\text{CO}_2$; $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$, and $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, if c , c_1 , c_2 , c_3 , c_4 are the concentrations of the water, hydrogen, oxygen, carbon dioxide, and carbon monoxide respectively, and K_1 , K_2 , K_3 the dissociation constants, then $c_2 c_4^2 = K_1 c_3^2$; $c_1 c_3 = K_2 c c_4$; and $c_1^2 c_2 = K_3 c^2$, whence $K_1 K_2^2 = c_1^2 c_2 / c^2 = K_3$, so that from the values of K_1 and K_2 the value of K_3 may be calculated. The value of K_1 at 1000° was calculated by Le Chatelier as $13 \cdot 10^{-13}$; the value of K_2 at the same temperature was found by Boudouard to be about 1.8, and for K_3 the value 5.2×10^{-12} results (Abstr., 1901, ii, 383). By the aid of the temperature coefficient for the heat of formation, the value at 20° is calculated as 5.7×10^{-78} , and the *E.M.F.* for the oxygen-hydrogen chain is found to be 1.15 volts, this number being in close agreement with the actual value, a result which the author considers tends to confirm the values of K_1 and K_2 .
L. M. J.

Amalgam Potentials. MAX REUTER (*Zeit. Elektrochem.*, 1902, 8, 801—808).—The author measures the *P.D.*'s between potassium amalgams and a solution of lithium chloride (1.56 per cent.) in methyl alcohol at about -80° . Amalgams containing less potassium than that indicated by the formula Hg_{12}K have a potential very little different from that of mercury. When the quantity of potassium is increased, the potential difference increases suddenly to 1.7 volts (compared with the hydrogen electrode). Further increase of the potassium gives a slow rise of *P.D.* until amalgams containing about 95 per cent. of potassium are reached when the *P.D.* rises quickly to that of pure potassium. The low *P.D.* observed with the amalgams containing little potassium is due to the formation of an external layer of solid mercury. This cannot occur with amalgams richer in potassium than Hg_{12}K , because they contain no uncombined mercury (Abstr., 1902, ii, 441, 638). The considerable depression of potential caused by addition of a small quantity of mercury is also found to occur in the case of sodium. The behaviour of the intermediate amalgams is consistent with the existence of other compounds of mercury and

potassium, although it gives no definite information as to their nature. T. E.

Anodic Decomposition Points of Aqueous Sodium Hydroxide Solutions. FRANZ PLZAK (*Zeit. anorg. Chem.*, 1902, 32, 385—403. Compare Bose, Abstr., 1899, ii, 348, and Glaser, *ibid.* 78).—The observations were made in a normal sodium hydroxide solution, with polished and platinised platinum electrodes, in a Bose cell; the cathode was saturated with hydrogen, and so also, in half of the experiments, was the anode. The *E.M.F.* was increased slowly and the galvanometer deflection was only observed after the polarisation current had become steady. The results are contained in the following table:

Cathode.	Anode.	Decomposition points.
(1) Polished	Polished: without hydrogen	1.08—1.09 volts.
(2) „	„ with „	1.08
(3) Platinised	„ without „	1.68
(4) „	„ with „	1.67
(5) „	Platinised: without „	1.075 and 1.53—1.54
(6) „	„ with „	1.08 and 1.53
(7) Polished	„ without „	0.87 (0.4)
(8) „	„ with „	(0.4) 0.90—0.91

In some of the curves, there are sudden changes of direction at two points, whilst in others the change of direction is only at one point.

When a polished and a platinised electrode are immersed in *N* sodium hydroxide solution, a potential difference of about 0.62 volt is established between them, the current passing through the electrolyte from the platinised to the polished electrode.

The decomposition points, 1.08 and 1.53 volts, observed when the electrodes are in the same condition, (1), (2), (5), (6), are the discharge potentials of the ions O'' and OH' . The points 1.68 volts, (3), (4), are due to the potential difference between the electrodes and the discharge potentials of the OH' ions. The values 0.4 and 0.9 volt, (7), (8), are due to the same cause as (3) and (4), but the potential difference between the electrodes acts here in the opposite direction.

J. McC.

Influence of Temperature on the Conductivity of Electrolytic Solutions. W. R. BOUSFIELD and T. MARTIN LOWRY (*Proc. Roy. Soc.*, 1902, 71, 42—54).—A discussion of the evidence bearing on the form of conductivity-temperature curves. The two factors which determine the form of these curves are (1) the increase of viscosity and decrease of the ionic mobilities with falling temperature; (2) the decrease of ionisation with rising temperature; and the temperature coefficient of conductivity will therefore be + or - according as one or other of these two factors predominates. It has been recently shown by Kohlrausch (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 42, 1026) that the conductivity-temperature curves for infinitely dilute solutions would, if produced, all cut the temperature axis within a

degree or two of -38.5° , a point which might be called the 'conductivity zero.' Kohlrausch shows also that a certain formula for the viscosity of water leads to an infinitely great viscosity at -38.5° , from which the relation between conductivity and viscosity is evident. The authors, however, consider that there is no such sharply defined limit to the conductivity, but that the conductivity-temperature curve approaches the temperature axis asymptotically.

The formula used by Kohlrausch and Déguisne to express the relation between conductivity and temperature was $K_t = K_{18} [1 + \alpha(t - 18) + \beta(t - 18)^2]$, and the authors now show, with the help of Thorpe and Rodger's data (*Phil. Trans., A.*, 1894, 185, 397—710), that the viscosity of water may be calculated with the analogous formula $\eta_{18} = \eta [1 + \alpha(t - 18) + \beta(t - 18)^2]$, the values of the coefficients α and β being very nearly the same as in the above conductivity formula when applied to water.

Just as there is a lower conductivity zero intimately connected with the viscosity, so there is probably an upper conductivity zero consequent on the decrease of ionisation with rising temperature. In aqueous solutions, the indications of such an upper limit are slight, for the temperature coefficient of conductivity is positive at the ordinary temperature and remains so up to the boiling point in almost all cases (phosphoric and hypophosphorous acids and copper sulphate are exceptions). Even between 0° and 18° , however, there is a decrease of ionisation (compare Whetham, *Phil. Trans.*, 1900, 194, 321), and Hagenbach has shown (*Abstr.*, 1901, ii, 434) that at high temperatures such salts as potassium chloride may have negative temperature coefficients of conductivity. In the case of non-aqueous solutions, there is much more evidence for the existence of an upper conductivity zero (compare Franklin and Kraus, *Abstr.*, 1900, ii, 645; Hagenbach, *loc. cit.*; Walden and Centnerszwer, *Abstr.*, 1902, ii, 245). The upper limit in the case of salt solutions would appear to be higher than for acid solutions, since the salts are capable of self-ionisation.

It follows from the above that the general curve expressing the effect of temperature on the conductivity of a composite electrolyte exhibits a maximum and has a point of inflexion on either side of this maximum. 'The authors' own work has demonstrated the existence of inflexion for solutions of lithium, sodium, and potassium hydroxides at about 40° , and for solutions of calcium, strontium, and barium hydroxides at about 25° . J. C. P.

Existence of Free Ions in Aqueous Solutions of Electrolytes. JULIUS OLSEN (*Amer. J. Sci.*, 1902, [iv], 14, 237—248).—The author discusses the experiment described by Ostwald and Nernst (*Abstr.*, 1889, 558) and shows that it is not conclusive.

When platinum foil electrodes are made so as fit the curvature of a beaker used as a cell and these are placed opposite to each other in a solution of sulphuric acid, a deflection is observed on a galvanometer connected to the electrodes; after standing, this deflection disappears. If an electrophorus disc be brought close to the cell, the galvanometer needle is deflected on account of the ordinary electrostatic induction. This was kept up for a considerable time by connecting the disc with the knobs of two Leyden jars charged by a

friction machine. A stationary state was established with the electrophorus disc placed parallel to a line joining the electrodes; the electrode system was then carefully turned through 90° so that a line joining them would be perpendicular to the disc. A different deflection was observed and this was due to an accumulation of one kind of ions in the cell near the charged disc. By rotation of the electrode system through 180° , the deflection was reversed. The same results were obtained with solutions of potassium hydroxide and potassium sulphate.

Two inner electrodes of platinum fastened together so that they could be rotated and two stationary electrodes fixed exactly opposite these were immersed in a solution of sulphuric acid. The two inner electrodes, about 50 mm. apart, were connected with a galvanometer, and the outer ones (at about 8 mm. distance from the inner) with a Daniell cell (*E.M.F.* smaller than the decomposition value). If the arrangement be denoted thus: $Aa\ a'A'$, A was connected to the positive pole of the Daniell cell when a was found to be negative. In a short time a became of the same sign as A , and by opening the cell circuit and rotating the inner system through 180° ($Aa\ a'A'$) the direction of the deflection was reversed, which shows that the liquid in the neighbourhood of the positive pole is charged with positive ions, or that around the negative pole the solution is charged with negative ions, or both.

The inner electrodes were rotated through 90° and a charged disc was brought up close to the cell in such a position that it was parallel to a line joining the electrodes AA' . The effect in this case was greater than when no current had been allowed to act on the solution.

Copper wires were placed in a solution of cupric sulphate and a decided deflection was observed when they were connected to a galvanometer; by bringing a charged disc up to one of these, the deflection was reversed. By closing the circuit for three-quarters of an hour, at the same time keeping up the charge on the disc, the cathode gained 1.2 mg. and the anode lost 0.4 mg. Similar results have been obtained with amalgamated zinc electrodes in a solution of zinc sulphate.

J. McC.

Conductivity of Solutions at Low Temperatures. J. KUNZ (*Compt. rend.*, 1902, 135, 788—790).—The conductivity of solutions of sulphuric acid from 19.1 to 63.76 per cent. have been determined from 0° down to -70° . The results obtained at 0° agree with those given by Bouty. The curves representing the conductivity as a function of the temperature do not meet the abscissæ axis at -39° as Kohlrausch (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1026) had predicted. The similarity of the curves indicates that the principal cause of the thermic radiation is the viscosity of the medium towards the ions. It is interesting to note that the resistance of metals approaches the value zero at 0° absolute, whilst the conductivity of electrolytes approximates to this value at the same temperature.

J. McC.

Migration Experiments to Determine the Constitution of Salts. ROBERT KREMANN (*Zeit. anorg. Chem.*, 1902, 33, 87—95).—**I. Cobaltamine Salts.**—When potassium diaminocobaltinitrite solution,

to which some sugar has been added, is placed in a U-tube with dilute sulphuric acid over it and a current of 0.2 ampere at 110 volts is passed through, the coloured layer passes in the direction of the anode; with purpureo-cobalt nitrate, it passes towards the cathode. This shows that the complex, coloured ion is an anion in the former case and a cation in the latter in agreement with Werner's view. The change of concentration on electrolysing chloropurpureo-cobalt nitrate was determined; the concentration of chlorine increases in the cathode liquid, whilst in the anode liquid it decreases. When potassium cobaltinitrite solution is electrolysed, the proportion of cobalt in the anode liquid is observed to increase.

II. *Methyl-orange*.—In strongly acid solution, no alteration of the position of the coloured layer with methyl-orange could be brought about on electrolysis, but in alkaline solution the coloured layer passes towards the anode. The author does not regard it as probable that methyl-orange acts as an amphoteric electrolyte.

III. *Salts of Cupriphosphorous Acid*.—When phosphorous acid is added to a copper salt solution, no precipitation takes place, and when the solution is electrolysed the coloured layer moves towards the anode. This suggests the migration of a complex, coloured ion (CuPO_3''), for if the compound formed were a double salt the coloured copper ion would wander towards the cathode.

IV. *Solutions of Chromium and Zinc Hydroxides in Alkalis*.—When a solution of chromium hydroxide in alkali is electrolysed, the coloured ion ($\text{Cr}_2\text{O}_2''$) migrates towards the anode, proving that the solution actually contains a chromite. When an alkaline solution of zinc hydroxide is electrolysed, the proportion of zinc at the anode increases; the anion therefore contains zinc, and consequently the solution must not be regarded as containing colloiddally dissolved zinc hydroxide.

J. McC.

Condition of Electrolytes in Aqueous Solution. ARTHUR HANTZSCH (*Chem. Centr.*, 1902, ii, 922; from *Verh. Vers. Deut. Natf. Aerzte*, 1901, 150—152).—Dimethylammonium chloride is soluble to the extent of 2.08 parts and 0.269 part in water and chloroform respectively; but when a concentrated aqueous solution is shaken with chloroform, scarcely any of the salt passes into the chloroform layer, which indicates that in the aqueous solution and in the chloroform solution there are different molecules. The concentrated aqueous solution contains up to 70 per cent. of undissociated salt, and the chloroform solution contains single as well as double molecules, consequently the abnormality cannot be attributed to a difference of molecular complexity. The explanation offered is that, in the aqueous solution, the salt exists as a hydrate which, as such, is insoluble in chloroform. The author suggests that in water all salts and their ions exist in the form of hydrates.

J. McC.

Conductivity of Certain Salts in Water, Methyl, Ethyl, and Propyl Alcohols, and in Mixtures of these Solvents. HARRY C. JONES and CHARLES F. LINDSAY (*Amer. Chem. J.*, 1902, 28, 329—370).—It has been shown by Zelinsky and Krapivin (*Abstr.*,

1897, ii, 5) that solutions of electrolytes in a mixture of equal quantities of methyl alcohol and water have a much smaller conductivity than in the pure alcohol. The authors have extended this work by determining the conductivity of solutions in which the solvents are mixtures of methyl alcohol and water in varying proportions, and have plotted curves showing, for each salt examined, the mixture of methyl alcohol and water which has the least dissociating power. They have also worked with ethyl alcohol, propyl alcohol, and with mixtures of ethyl alcohol and water, propyl alcohol and water, and methyl and ethyl alcohols. The experiments were carried out at 0° and 25° , and in this way it was possible to calculate the temperature coefficients of conductivity of the various salts in the different solutions, and to show the influence of temperature on the minimum values mentioned above. The salts employed were potassium iodide, strontium iodide, ammonium bromide, cadmium iodide, lithium nitrate, and ferric chloride.

In the case of potassium iodide, the molecular conductivity at 0° reaches a minimum in a mixture of methyl alcohol and water containing 50 per cent. of methyl alcohol; a solution in a mixture containing about 10 per cent. of methyl alcohol has the same conductivity as a solution in the pure alcohol. At 25° , the minimum conductivity is obtained in a mixture containing 65 per cent. of methyl alcohol, and the mixture, which has the same conductivity as the solution in pure methyl alcohol, contains about 30 per cent. of the alcohol. The conductivity of potassium iodide in a 50 per cent. mixture of methyl and ethyl alcohols shows no minimum value either at 0° or 25° when compared with the conductivity in the pure solvents, but the conductivity of a solution in the mixed solvents always lies below the mean value of the conductivities in the pure solvents.

The minimum point in the conductivity values at 0° of solutions of ammonium bromide in mixtures of methyl alcohol is reached with alcohol of 50 per cent. strength. A 50 per cent. ethyl alcohol solution also gives a minimum conductivity, but only in the case of dilute solutions ($v=512$ or 1024). A mixture of methyl and ethyl alcohols gives no minimum value.

With solutions of strontium iodide at 0° , the minimum point is reached, as in the previous cases, with methyl alcohol of 50 per cent. strength. At 25° , the minimum occurs with alcohol of about 65—70 per cent. In mixtures of ethyl alcohol and water, a minimum is obtained at 0° in a solution where $v=1024$, but at 25° there is no trace of a minimum point although the values are well below the mean values for the pure solvents. With a mixture of propyl alcohol and water, no minimum is obtained either at 0° or 25° .

In the case of cadmium iodide, a minimum point is not reached with mixtures of methyl alcohol and water either at 0° or 25° , but the conductivity values are always lower than those required by the law of mixtures.

The curves obtained with lithium nitrate are similar to those obtained with potassium iodide and strontium iodide. It is, however, noteworthy that at 0° the molecular conductivity in pure methyl alcohol rises above that in water.

In solutions of ferric chloride, hydrolysis was found to occur, accompanied by a steady rise in the molecular conductivity.

The following considerations are put forward to explain the phenomena described in this paper.

Dutoit and Aston (*Abstr.*, 1897, ii, 546) have expressed the view that only associated solvents are capable of dissociating dissolved electrolytes. Since the substances which produce such dissociation show, generally, a normal molecular weight for dissolved non-electrolytes, it is probable that the breaking down of the polymerised molecule can be best accomplished by means of the associated molecule of another substance. Hence it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water with methyl alcohol or ethyl alcohol, or a mixture of methyl and ethyl alcohols, and since the molecules in such mixtures are less associated than in the original constituents, the conductivity of dissolved electrolytes would, as has been shown to be the case, be lower than that required by the law of mixtures. E. G.

Influence of the Solvent in Electrolytic Conduction.
HARRISON EASTMAN PATTEN (*J. Physical Chem.*, 1902, 6, 554—600).—The author first determined the effect of the addition of various solvents on the specific conductivity of a solution containing 17 per cent. of pyridine and 83 per cent. of acetic acid. The compounds added were benzene, toluene, xylene, cymene, naphthalene, amylene, water, methyl alcohol, ethyl alcohol, acetone, methyl acetate, methyl nitrate, isobutyl nitrate, chloroform, carbon tetrachloride, bromoform, ethyl bromide, propyl bromide, amyl bromide, ethylene bromide, butylene bromide, methyl iodide, ethyl iodide, amyl iodide, benzonitrile, nitrobenzene, benzaldehyde, amyl hydrosulphide, and ethyl xanthate. Similar experiments were also made with a *N*/10 solution of silver nitrate in pyridine. With the exception of water in the first set, and methyl alcohol in dilute solution in both sets, the addition in all cases produces a lowering of conductivity, this being proportional to the concentration up to concentrations of about 40 per cent. The author states that for analogous substances this lowering is roughly proportional to the number of gram-molecules of diluent added, but the numbers recorded in the tables hardly warrant this generalisation. The lowering of the specific conductivity is proportional neither to the dielectric constant nor to its coefficient of association, nor does it appear to bear any relationship to these properties. The author considers that the results do not accord with the dissociation theory, and the numbers obtained for the dissociation from the conductivity experiments and from cryoscopic observations are not concordant. The author considers the conduction of electricity by solutions to depend on the formation of a compound by the solvent and solute, and the degree of conductivity to depend on the constituents of this compound and possibly on their arrangement. L. M. J.

Solubility, Electrolytic Conductivity, and Chemical Action in Liquid Hydrogen Cyanide. LOUIS KAULENBERG and HERMAN SCHLUNDT (*J. Physical Chem.*, 1902, 6, 447—462).—Experiments were

made on the electrolytic conductivity of solutions of a great number of compounds in liquid hydrogen cyanide. Over 100 compounds were thus investigated qualitatively, and quantitative observations are recorded for 24 compounds. Potassium salts yielded solutions of very high conductivity, which, in the case of the iodide and nitrate, is over 3.5 times as great as that of the corresponding aqueous solution. Ammonium chloride and silver sulphate also form solutions of higher conductivity than the aqueous. Acids, however, form solutions of far lower conductivity than the corresponding aqueous solutions; silver nitrate, ferric chloride, antimony, and bismuth chloride also form comparatively feeble conducting solutions. Amylamine, strychnine, and morphine form solutions of high conductivity. The author considers that these results indicate that the conductivity of a solution is not determined by its dielectric constant or spare valencies, but depends on mutual action of solute and solvent. A number of reactions were also investigated in liquid hydrogen cyanide; it does not react with sodium carbonate; a solution of sulphur trioxide did not act on magnesium or on carbonates; a solution of fuming sulphuric acid attacked magnesium and zinc, but not iron, aluminium, or calcium carbonate, and somewhat similar results were obtained with hydrogen chloride.

L. M. J.

Behaviour of some Alloys in Regard to the Law of Wiedemann and Franz. F. A. SCHULZE (*Ann. Physik.*, 1902 [iv], 9, 555—589).—The thermal and electrical conductivities for alloys of bismuth and lead vary with the composition in a similar manner, the addition of a small quantity of lead causing a rapid fall of both conductivities below the values for pure bismuth; on further addition of lead, the conductivities slowly increase to the values for pure lead. The values of the conductivity (both thermal and electrical) found by experiment are always less than those calculated from the proportion by volume in which the metals are present. What has been said for alloys of bismuth and lead applies also to alloys of bismuth and tin.

For alloys of zinc and tin, on the other hand, the thermal and electrical conductivities observed are very nearly those calculated from the proportion by volume in which the metals are present. J. C. P.

Extrapolation of the Melting Point of a Chemically Homogeneous Substance from Measurements of the Volume in the Neighbourhood of the Melting Point. VALENTINE SOBOLEFF (*Zeit. physikal. Chem.*, 1902, 42, 75—80).—If Δv be the alteration of volume of the pure compound during melting, which can be sufficiently approximately obtained from impure material, and if in a compound containing impurity of concentration x the volumes are determined at three temperatures, T_1 , T_2 , T_3 , in each of which the substance is partially melted, solid and liquid being in equilibrium, then

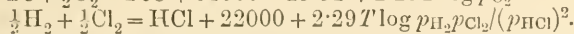
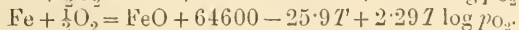
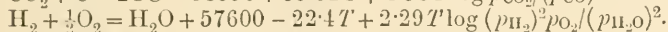
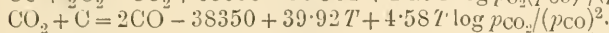
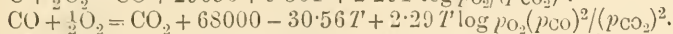
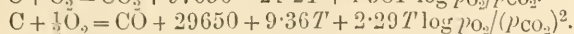
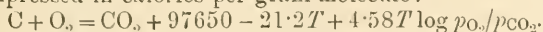
$$(T'_0 - T_1)/x(\Delta v/\Delta v_1) = (T'_0 - T_2)/x(\Delta v/\Delta v_2) = (T'_0 - T_3)/x(\Delta v/\Delta v_3) = \text{constant.}$$

This leads to $T'_0 = (\Delta v_1 T_1 - \Delta v_2 T_2)/(\Delta v_1 - \Delta v_2)$. In the case of a sample of diphenylamine which crystallised between 52.4° and 51.5° ,

the melting point was thus found to be $54.32^\circ \pm 0.26^\circ$, whilst in another, which crystallised between 51.9° and 50.8° , the melting point was calculated at $54.19^\circ \pm 0.41^\circ$. The melting points of *o*-cresol, naphthalene, and vanillin were thus calculated and found to be in each case slightly higher than that given in chemical literature as the melting point of the pure compound.

L. M. J.

Theory of some Technical Processes of Reduction and Oxidation. GUIDO BODLÄNDER (*Zeit. Elektrochem.*, 1902, 8, 833—843).—The author calculates the free energy of several reactions at absolute temperature T , the following being the most important results expressed in calories per gram-molecule:



Common logarithms are to be used, p_{O_2} , p_{CO_2} , &c., standing for the pressures (in atmospheres) of the gaseous substances in equilibrium at T . It is shown that these values are in good agreement with the reactions observed in water-gas producers, blast furnaces, and Bessemer converters in the reduction of zinc oxide, in the Deacon chlorine process, and in other processes.

T. E.

Distillation of Binary Mixtures. LORD RAYLEIGH (*Phil. Mag.*, 1902, [vi], 4, 521—537).—The author considers how, for a given total pressure, the composition of the vapour given off from a binary liquid mixture may be related to the composition of the latter. The relation may be expressed on a square diagram by a curve joining the opposite corners of the square, the composition of the liquid being measured horizontally and the corresponding composition of the vapour vertically. The author discusses and deduces in a new way Konowaloff's theorem that any mixture which corresponds with a maximum or minimum vapour pressure has (at the temperature in question) the same composition as its vapour.

The corresponding compositions of liquid and distillate have been determined for mixtures of alcohol, hydrogen chloride, ammonia, sulphuric acid, and acetic acid with water.

A new apparatus with uniform *régime*, illustrating the principles of ideal distillation, has been constructed and found to effect a very satisfactory separation of water and alcohol in one operation.

J. C. P.

Molecular Weight Determinations of Solid and Liquid Substances in the Weinhold Vacuum Vessel. HUGO ERDMANN and MAX VON UNRUH (*Zeit. anorg. Chem.*, 1902, 32, 413—424).—Instead of using the ordinary tube in Landsberger's apparatus for determining

the rise of boiling point, a vacuum vessel such as is used for working with liquefied gases has been employed. Experiments with carbon disulphide as solvent show that extremely good results can be obtained by this process. The authors give the following constants for various solvents :

	<i>K</i> for 100 grams	<i>K</i> for 100 c.c.
Water.....	520	542
Ethyl alcohol	1150	1558
Acetic acid.....	2530	2699
Acetone.....	1670	2225
Ethyl acetate.....	2610	3154
Ethyl ether	2110	3036
Ethylene bromide	6320	3284
Benzene	2670	3288
Phenol	3040	3587
Aniline	3220	4026
Chloroform.....	3660	2528
Carbon disulphide	2370	1940

J. McC.

Ebullioscopic Relations of Volatile Substances; Molecular Weight of Inorganic Chloroanhydrides and of Iodine. Reply to Ciamician. I. GIUSEPPE ODDO (*Gazzetta*, 1902, 32, ii, 97—106).—A reply to the criticisms of Ciamician (*Abstr.*, 1902, ii, 123) on the author's work in this direction (*Abstr.*, 1902, ii, 6).

T. H. P.

Ebullioscopic Relations of Volatile Substances. Experimental Method used by Ciamician. II. GIUSEPPE ODDO (*Gazzetta*, 1902, 32, ii, 107—122. Compare preceding abstract).—The author has applied Beckmann and Stock's ebullioscopic method (*Abstr.*, 1895, ii, 382), which was used by Ciamician in the measurement of the molecular weights of volatile compounds (*loc. cit.*), to the examination of solutions of chloroform in ether, iodine in carbon tetrachloride, alcohol, chloroform, carbon disulphide, or benzene, and of phosphorus oxychloride in benzene, carbon tetrachloride, chloroform, or carbon disulphide. The influence exerted by the presence of small quantities of the more common impurities in various solvents, such as water in alcohol and alcohol in benzene, has also been investigated. From the results obtained, the author concludes that Beckmann and Stock's method, consisting in measuring separately the rise in boiling point of the solvent and the concentration of the dissolved substance in the vapour, is erroneous and fallacious.

T. H. P.

Ordinary Ebullioscopic Method and Apparatus. GIUSEPPE ODDO (*Gazzetta*, 1902, 32, ii, 123—138. Compare two preceding abstracts).—This paper, which is also written in reply to Ciamician (*loc. cit.*), contains a description of an apparatus which allows of the measurement, with one and the same solution, of the increase of boiling point and of the concentration of the solute in the vapour. This apparatus, which can be employed for the ebullioscopic examination of

volatile solutes, is applied to the following four cases : (1) non-volatile compounds, or those nearly so, such as dimethylaniline in benzene or alcohol and β -naphthyl benzoate in carbon tetrachloride. (2) Volatile substances which boil at a higher temperature than the solvent and raise the boiling point of the latter. Of such were examined, epichlorohydrin, isopropyl iodide, and phosphorus oxychloride in benzene, phosphorus oxychloride in carbon tetrachloride, and iodine in benzene, alcohol, or carbon tetrachloride. (3) Volatile substances which boil at a lower temperature than the solvent and lower its boiling point. The cases investigated were : ethyl iodide and phosphorus trichloride in benzene. (4) Substances which boil at a higher temperature than the solvent but which lower the boiling point of the latter. This is the case with a solution of isopropyl iodide in alcohol, and the numbers obtained for the molecular weight of the iodide are very irregular. T. H. P.

Differential Method of Determining Small Freezing Point Depressions. HERBERT HAUSRATH (*Ann. Physik.*, 1902, [iv], 9, 522—554).—The apparatus consists essentially of two freezing vessels placed side by side in a box, which is immersed completely in the cooling bath. One freezing vessel contains pure water, the other the solution the freezing point of which is to be determined ; the difference between the freezing temperatures in the two vessels is determined thermoelectrically to within a few hundred thousandths of a degree.

The solutes used were carbamide, sucrose, alcohol, lead and barium nitrates, copper, zinc, magnesium, nickel and cadmium sulphates, sodium and hydrogen chlorides, sulphuric acid, potassium hydroxide, acetic and dichloroacetic acids, and the molecular depression has been calculated for each solution. Carbamide was taken as the normal substance, and from five series of thirty-three determinations for solutions varying in concentration from 0.0005—0.04*N* the mean value of the molecular depression was 1.85, the individual values (with three exceptions) lying between 1.836 and 1.866. The molecular depression for sucrose solutions was found to be 1.872, although for the greatest dilutions a somewhat greater value was obtained. Alcohol gave irregular and abnormally small values—down to 1.60. It was thought that in the case of the salts of heavy metals, such as lead and copper, the effect of hydrolytic dissociation would be evident in the most dilute solutions, but this was not so ; thus the depressions for lead nitrate ran parallel to those for barium nitrate, and the depression-concentration curve for copper sulphate was coincident, at least for the more dilute solutions, with those for zinc and magnesium sulphates. In the case of the strong electrolytes, the values of the molecular depression for the most dilute solutions are much below 3.70, but it is noticeable that the number increases with the concentration, reaching a maximum at about 0.007*N* ; the author considers that this remarkable result cannot be attributed to the errors in the method employed, and notes that it is in conflict with the ionic theory. J. C. P.

New Method of Determining the Vapour Density of Metallic Vapours, and an Experimental Application to the Cases of Sodium and Mercury. FRANK B. JEWETT (*Phil. Mag.*, 1902, [vi], 4, 546—554).—In order to prepare for a study of the effect of pressure

and temperature on the broadening of the spectral lines in the case of sodium and mercury (compare Michelson, *Phil. Mag.*, 1892, [v], 34, 293) and to discover the relation of the change in the lines in the Zeeman effect to the density of the light-producing vapour, the density of saturated sodium vapour has been determined from 368° to 420° and that of mercury from 40° to 325°. In the case of sodium, a two litre globe was filled with an inert gas and exhausted. A side tube containing sodium had been previously sealed on, and when the whole was placed in a large air-bath heated to a constant temperature by means of resistance coils, the globe became filled with sodium vapour. On cooling, the metal was deposited on the interior surface of the globe and was then estimated by analysis. In the case of mercury, the amount of metal which had entered the globe was deduced from the diminution of the mercury in the side tube. The values obtained for the density of mercury vapour agree fairly well with those of earlier observers. J. C. P.

Determination of Vapour Density under Diminished Pressure. HUGO ERDMANN (*Zeit. anorg. Chem.*, 1902, 32, 425—430).—The side tube of a Victor Meyer apparatus is connected with a manometer and with a pump. After temperature-equilibrium has been established and the pressure reduced, the weighed quantity of substance is dropped in and the pressure measured on the manometer. The constant for the apparatus is determined by carrying out the experiment with a substance of known molecular weight.

Results obtained with this apparatus show that the two substances of melting points 82—84° and 153—154.5°, obtained by polymerisation of phenylacetaldehyde, dissociate to simple molecules, C_8H_8O , when volatilised. The hydrates of nitric acid described in this vol., ii, 73, suffer dissociation, which is complete at 95°. J. McC.

Dialysis Experiments with Metallic Hydroxides. WALTER HERZ (*Zeit. anorg. Chem.*, 1902, 32, 357—358. Compare Abstr., 1902, ii, 608).—Stannic hydroxide and antimonious hydroxide, in presence of alkali, when placed in a dialyser pass through the membrane; these, therefore, like stannous hydroxide, are to be classed as acids which form salts with alkalis.

If zinc hydroxide be dried at 60—70°, and then dissolved in sodium hydroxide solution, the zinc passes through the membrane. The same takes place with dried beryllium hydroxide. Since zinc hydroxide, freshly precipitated, behaves differently (*loc. cit.*), it is concluded that a chemical change takes place on drying. Whether the change is one of dehydration or of allotropism cannot yet be decided.

When an ammoniacal solution of zinc hydroxide is placed in a dialyser, the zinc passes through the membrane; an ammoniacal solution of chromic hydroxide behaves in the same way. J. McC.

Theory of the Capillary Film between the Homogeneous Phases of Liquid and Vapour. II. G. BAKKER (*Zeit. physikal. Chem.*, 1902, 42, 68—74).—A mathematical paper on the thickness of this capillary film (compare Abstr., 1901, ii, 374). L. M. J.

Modern Theories of Solution. The Osmotic Theory and the Theory of Electrolytic Dissociation. ISIDOR TRAUBE (*Chem. Zeit.*, 1902, 26, 1071—1074).—Although van't Hoff's laws for dilute solutions cannot be doubted, and although the benefits conferred by the Arrhenius theory of electrolytic dissociation are fully recognised, the author objects to too close an analogy being drawn between gases and dilute solutions. An acceptable theory of solution must account for the part played by the solvent. In concentrated aqueous solution, the results interpreted by the theory from the observed conductivities do not agree with the law of mass action, and in solvents other than water the osmotic results and the conductivity results lead to opposite conclusions. The author believes that a combination of the Clausius hypothesis with the "hydrate" theory will give the best explanation of the nature of solutions.

J. McC.

Numerical Examples of the New Theory of Solutions. J. B. GOEBEL (*Zeit. physikal. Chem.*, 1902, 42, 59—67).—An expression has been deduced by Nernst in which the dissociation constant is equal to $(c_2^2/c_1)e^{2c_2(a_2+a_{23}-a_{12})+c_1(2a_{12}-a_1)}$, where a is a coefficient due to the inter-influence of the neutral molecules, a_2 and a_{23} similar coefficients due to the ions, and a_{12} that due to the influence of ion on non-electrolyte. The author shows that this is in complete accord with the experimental determinations of the freezing point depressions in the case of sodium and potassium chlorides.

L. M. J.

Solid Solutions. GIUSEPPE BRUNI [with L. MASCARELLI and M. PADOA] (*Atti Real. Accad. Lincei*, 1902, [v], 11, ii, 187—195).—The authors' investigations have been made with the object of determining the analogies of constitution which induce the formation of solid solutions of two compounds and of seeing whether organic substances show the same relations of isomorphism and formation of mixed crystals as are observed in the case of inorganic compounds and *vice versa*. The results obtained, showing the influence of substitution of certain isomorphogenous atoms or atomic groups, are as follows:

I. H, OH.—Dimethyl malate, *d*-tartrate, and racemate exhibit a perfectly normal cryoscopic behaviour in methyl succinate solutions; the same is the case with inactive mandelic acid when dissolved in the corresponding phenylacetic acid. The tendency of organic substances to form mixed crystals with their hydroxyl derivatives, in which the hydroxyl groups are united to an open chain, is hence not a perfectly general one, but such a formation of mixed crystals can take place when the molecular weights of the compounds are high, as is shown by the abnormal cryoscopic behaviour of hydrobenzoin and isohydrobenzoin in dibenzyl solution. Hydroxylamine alum and ammonium alum also form mixed crystals; slightly abnormal molecular weights are exhibited by *p*-tolylhydroxylamine in *p*-toluidine and by α -naphthylhydroxylamine in α -naphthylamine.

II. H, OH, NH₂.—Slightly anomalous behaviour is shown by *p*-toluidine in *p*-cresol solution, whilst with α -naphthol in α -naphthylamine and *s*-tribromoaniline in *s*-tribromophenol very abnormal

weights are obtained. These results show that, in general, hydroxyl compounds form mixed crystals with the corresponding amino-derivatives. The value $K=204$ for the freezing point constant of *s*-tribromophenol is the highest yet obtained for organic solvents.

III. CH_2N , N .—In azoxybenzene solution, the phenyl derivative of benzaldoxime, $\text{O} \begin{smallmatrix} \text{NPh} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{HPh} \end{smallmatrix}$, exhibits very abnormal cryoscopic behaviour, and the same is the case with benzylideneaniline dissolved in azobenzene. The first pair of compounds may be regarded as derived from phenylhydroxylamine by its combination with nitrosobenzene and benzaldehyde respectively, and the second pair as derived from aniline by combination with benzaldehyde and nitrosobenzene respectively. Since, however, benzaldehyde and nitrosobenzene, as well as their immediately higher homologues, do not lend themselves to cryoscopic examination, ethyl *o*-nitrosobenzoate was tested in solution in ethyl phthalaldehyde, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$, and was found to yield solid solutions with the solvent. In *s*-trichlorobenzene solution, cyanuric chloride exhibits normal cryoscopic behaviour, but no conclusions can be drawn from this with regard to the constitution of the cyanuric compounds.

IV. $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$, $\cdot\text{CH}\cdot\text{CH}\cdot$, $\cdot\text{C}\cdot\text{C}\cdot$.—Cryoscopic measurements of methyl acetylenedicarboxylate in methyl succinate, of phenylpropionic acid in phenylpropionic acid, and of methyl phenylpropionate in methyl cinnamate show that these pairs of compounds form solid solutions. Hence acetylene derivatives crystallise together with the corresponding saturated compounds and with those having a fumaroid structure and derived from ethylene.

The author discusses the isomorphism existing between inorganic compounds differing in the possession of two atoms of fluorine in place of one of oxygen or one of fluorine instead of a hydroxyl group. To see whether any similar relations exist between organic compounds, the cryoscopic behaviour of phthalic anhydride dissolved in phthalic chloride was examined, very abnormal molecular weights being obtained. Quinol and *p*-dichlorobenzene do not crystallise together, but when β -naphthol is dissolved in β -chloronaphthalene the freezing point of the latter is raised.

T. H. P.

Solubilities of some Carbon Compounds and Densities of their Solutions. CLARENCE L. SPEYERS (*Amer. J. Sci.*, 1902, [iv], 14, 293—302).—The same solvents and dissolved substances were used as in the determination of the heats of solution (Abstr., 1896, ii, 410) and molecular weights in concentrated solution (Abstr., 1902, ii, 388). With the exception of urethane in water and chloral hydrate in chloroform, the solubility curves are all regular. In these two cases, there is a sudden change of direction at about 12° , showing a rapid decrease in solubility as the temperature falls below this point.

The variations of solubility in passing from one solvent to another are shown graphically. No regularity in change of solubility as the molecular weight of the alcoholic solvents increases can be noticed. The results are not in agreement with the equation deduced by Schroeder (Abstr., 1893, ii, 366). The densities of the saturated

solutions have also been determined and with the aid of these the osmotic pressures have been found. The osmotic pressure is not constant for each dissolved substance, and from this it is deduced that the analogy between solution and vaporisation is far from complete.

The molecular volumes of the dissolved substances are greater in water than in other solvents, and in these they decrease in the order: methyl alcohol, ethyl alcohol, propyl alcohol, toluene, chloroform. In general, the molecular volumes of the dissolved substances decrease as the temperature and concentration increase. J. McC.

Solubility of Salts of Optically Active Monobasic Acids. CÆSAR POMERANZ (*Monatsh.*, 1902, 23, 747—749).—A mathematical discussion of the relationship between the solubility of the silver salts of an optically active monobasic acid and of the mixture of the salts of the *d*- and *l*-acids. The equation $L = \sqrt{2}l$ is established, where L is the solubility of the mixture, and l that of either the *d*- or *l*-forms. Taking the non-dissociated portions into account, this becomes $L = \{2(1 - a) + \sqrt{2}a\}$. The formula is applied to silver *d*-valerate.

E. F. A.

Method for the Calculation' of Solubilities. ALEXANDER FINDLAY (*Zeit. physikal. Chem.*, 1902, 42, 110—112; see Abstr., 1902, ii, 386).—An extension of the previous paper. L. M. J.

Acids of Phosphorus. Reaction between Phosphoric Acid and Mercuric Chloride. III. CLEMENTE MONTEMARTINI and U. EGIDI (*Gazzetta*, 1902, 32, ii, 182—196. Compare Abstr., 1901, ii, 551, and 1902, ii, 451).—The authors have investigated the reaction $2\text{HgCl}_2 + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} = 2\text{HgCl} + 2\text{HCl} + \text{H}_3\text{PO}_4$, in which, assuming the mass of water acting as solvent to be constant, 3 mols. of two different compounds react together. The object was to ascertain whether the reaction is of the second or third order, and whether its course is disturbed by the heterogeneity brought about by the precipitation of the mercurous chloride. The conclusion is arrived at that, in very dilute solution, the reaction is one of the third order, but that it is subjected to a very large initial disturbance, which can to some extent be removed by the presence in the liquid of a large quantity of added mercurous chloride. The initial addition of hydrochloric acid to the reacting solutions results in a disturbance of the reaction, which is at first much retarded.

If the mercuric chloride and phosphorous acid are not employed in the proportions indicated by the above equation, but are taken either in molecular proportions or in the ratio $4\text{HgCl}_2 : \text{H}_3\text{PO}_3$, the reaction may be regarded equally well as of the second or third order.

T. H. P.

Equilibrium between Maltose and Dextrose. CÆSAR POMERANZ (*Monatsh.*, 1902, 23, 750—753).—The author applies the mass law to the case of the reversible hydrolysis of maltose by maltase, studied by Croft Hill (*Trans.*, 1898, 73, 634), and shows that, as required, the

(concentration dextrose)²/concentration maltose is approximately a constant.
E. F. A.

Catalysis and Catalysers. MAX BODENSTEIN (*Chem. Zeit.*, 1902, 26, 1075—1079).—The author reviews the various suggestions which have been brought forward to explain catalysis. A catalyser is a substance which accelerates a reaction by its presence, but it cannot introduce a reaction which is not already taking place, and it cannot disturb an equilibrium. Liebig's theory is discussed; although it is not contrary to the laws of thermodynamics, it offers no advantage. The explanation which assumes the formation of intermediary products is also discussed; this is a plausible explanation, but because the catalyser is able to enter into reaction with one of the reacting substances under special conditions, the conclusion must not at once be drawn that this offers a satisfactory explanation of the acceleration by the catalyser. Reference is made to Euler's theory that all reactions are ionic and the acceleration is due to the catalyser causing an increased ionisation. The several theories may fit various cases of catalysis, and it is highly improbable that one theory will be sufficient to cover the various groups of catalytic phenomena.

The advantage of catalysers for industrial processes is pointed out.
J. McC.

Catalysis of Salts of Peracids. L. PISSARJEWSKY (*Zeit. anorg. Chem.*, 1902, 32, 341—346).—The catalysis of the hydrogen peroxide in solutions of sodium perborate and potassium pervanadates was determined in a conductivity vessel with platinised platinum plates. At the same time, the concentration of hydrogen peroxide in the solutions was determined by shaking out with ether. At 25°, the distribution-ratio of hydrogen peroxide between water and ether is 0.0625. In *N*/142.5 solution, the salt $K_8V_5O_{26}$ is dissociated to such an extent that 1.7 per cent. of the hydrogen peroxide is present in the free state. In *N*/15 solution, the salt KVO_4 is dissociated to the extent of 5.1 per cent., and the perborate $NaBO_3$ to 59.6 per cent. Half of the hydrogen peroxide from the salt $K_8V_5O_{26}$ is decomposed in the cell in 1566 minutes, from the salt KVO_4 in 618 minutes, and from the perborate $NaBO_3$ in 33 minutes. The speed of decomposition by the catalyser decreases as the concentration of free hydrogen peroxide increases.

J. McC.

Molecular Lowering of the Crystallisation-velocity by the Addition of Foreign Compounds. EDGAR VON PICKARDT (*Zeit. physikal. Chem.*, 1902, 42, 17—49).—It is shown that the addition of impurities lowers the velocity of crystallisation of benzophenone and benzoic anhydride. The lowering is not proportional, however, to the concentration, but to the square root of the concentration of the added compound; it is, however, independent of the nature of the compound, equal numbers of molecules producing equal lowering. It is clear that the lowering of the velocity depends on the original purity of the compound; thus if a compound contains

originally 1 per cent. of impurity (molecular concentration), the addition of 1 per cent. will cause an apparent lowering of only $(\sqrt{2} - \sqrt{1})k$, that is, of about $0.4k$. On this account, it is necessary either to obtain absolutely pure compounds or to extrapolate from numerous results. The latter is the only practical method, and is that used by the author; the crystallisation-velocity of the purest benzophenone obtainable was 59.5 mm. per minute, that of the absolutely pure benzophenone is calculated to be 61.5 mm. per minute. The constant is found to be 17.1, so that the material employed contained 0.0137 molecules of impurity per 100 molecules of benzophenone. Concordant results were obtained with twenty-six different compounds, but the addition of azobenzene, dinitrobenzene, and nitrobenzaldehyde led to results which indicated that condensation takes place in these compounds in the ratio 2 : 1, with nitrotoluene the indicated condensation is 3 : 1, and for quinone 4 : 1. In the case of resorcinol, dissociation takes place, or a reaction producing a doubled number of molecules. Experiments on the effect of the addition of mixtures proved the lowering to be colligative and given by the formula $L = k\sqrt{c_1 + c_2 + \dots}$. Analogous results were obtained in the case of benzoic anhydride, but the constant is only 7.85. It is evident that the determination of the lowering of crystallisation-velocity affords a means of obtaining the molecular weight of the solute.

L. M. J.

The Nature of the Metallic Condition. HUGO ERDMANN (*Zeit. anorg. Chem.*, 1902, 32, 404—406).—The different behaviour of metals and non-metals is supposed to be due to the metals being elements the molecules of which consist of single atoms, whilst the molecules of non-metals consist of several atoms. An analogy is drawn between Dulong and Petit's law and Avogadro's. The reactivity of the metals is attributed to their monoatomicity.

J. McC.

Negative Nature of Unsaturated Radicles. DANIEL VORLÄNDER (*Ber.*, 1902, 35, 4142—4146).—Controversial in reply to Henrich (this vol., ii, 16).

T. M. L.

Influence of Bridge-linking on Asymmetry. ZDENKO H. SKRAUP (*Ber.*, 1902, 35, 3981—3984).—As a result of the study of models of cyclic compounds having a bridge-linking and one or more asymmetric carbon atoms, it is seen that when the bridge joins two asymmetric carbon atoms, the number of possible stereoisomerides is only half what is generally the case. This holds whatever be the number of atoms in the 'bridge' or the position of the two asymmetric carbon atoms relatively to each other.

This fact is very well illustrated in the case of Brecht's formula for camphor; here the 'bridge' joins the two asymmetric carbon atoms and only two stereoisomerides are possible. In the case of Koenigs' cinchonine formula, the bridge does not join any two of the three asymmetric carbon atoms present; consequently eight stereoisomerides are possible (compare Aschan, this vol., ii, 2).

K. J. P. O.

Stereochemistry of Dicyclic Systems. PAUL JACOBSEN (*Ber.*, 1902, 35, 3984—3988. Compare this vol., ii, 2).—The view put forward by Skraup (preceding abstract), that the joining by means of a 'bridge' of two asymmetric carbon atoms in a cyclic compound limits the number of stereoisomerides, is criticised. For example, methylhexahydrophthalic acid exists in four forms, each of which yields an anhydride; these anhydrides are dicyclic compounds. Why should not therefore the dicyclic ketone, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} - \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \end{array} > \text{CO}$, exist in four active forms? According to Skraup, there should only be two.

K. J. P. O.

Fourth Report of the Committee [of the German Chemical Society] on Atomic Weights. HANS LANDOLT, WILHELM OSTWALD, and KARL SEUBERT (*Ber.*, 1902, 35, 4028—4030. Compare Abstr., 1899, ii, 86; 1900, ii, 533; 1902, ii, 129).—A limited international committee (F. W. Clarke, T. E. Thorpe, and K. Seubert) has been appointed to consider the preparation and issue of tables of the correct atomic weights.

K. J. P. O.

Inorganic Chemistry.

Atmospheric Hydrogen. ANATOLE LEDUC (*Compt. rend.*, 1902, 135, 860—861. Compare Rayleigh, Abstr., 1901, ii, 141, and 1902, ii, 391; Gautier, Abstr., 1900, ii, 538).—The amount of oxygen in the air, determined directly, should agree with that calculated from the density of oxygen and atmospheric "nitrogen" if Dalton's law of partial pressure holds and if the air contains no such gas as hydrogen, which would affect the value of the density of the "nitrogen" prepared by means of copper. The quantities of oxygen found were 23.18 to 23.23 per cent., whereas that calculated was 23.22 per cent. But Gautier found 0.02 per cent. of hydrogen, which would lead to 23.36 per cent. of oxygen by calculation. If, on the other hand, Rayleigh's value for hydrogen, 0.006 per cent., be taken, the calculated percentage of oxygen is 23.23, which agrees closely with that found.

K. J. P. O.

Preparation of Pure Hydrogen. MAURICE VÈZES and J. LABATUT (*Zeit. anorg. Chem.*, 1902, 32, 464—468).—The authors describe a form of apparatus suitable for the production of pure hydrogen by the electrolysis of 30 per cent. sodium hydroxide solution with nickel plate electrodes; about 20 c.c. of hydrogen are produced per minute and can be drawn off for use at practically constant pressure. An *E.M.F.* of 110 volts should be used.

J. McC.

Purification of Waters containing Silica and Magnesia. ORAZIO REBUFFAT (*Gazzetta*, 1902, 32, ii, 173—178).—From the results of a number of experiments on the treatment of waters containing silica and magnesia, the author draws the following conclusions: (1) in water in which silica, magnesia, and chlorine are present, only a small proportion of the magnesia is precipitated when the hydrogen carbonates are decomposed, either by boiling or by treatment with calcium hydroxide in the cold. Total precipitation of the magnesium can only be effected by means of lime. (2) The precipitation of the silica only takes place after the complete removal of the magnesia, and such precipitation is only complete in presence of a certain amount of free lime in the liquid and is probably preceded by the total separation of the carbon dioxide. (3) The treatment of such waters for complete purification should be carried out in two phases. In the first, the water is treated in the cold with an excess of lime, and in the second the resulting liquid is acted on either with sodium carbonate or, more economically, with a quantity of carbon dioxide just sufficient to precipitate the excess of lime present.

Attention is called to a source of error existing in the estimation of the solid matter present in a water containing appreciable quantities of silica. The hydrated silica does not give up the main portion of its water at temperatures lower than 180° . If, however, the residue from the evaporation of the water is dried at this temperature, there can be no doubt that a smaller error in the opposite direction is caused by the evolution of carbon dioxide brought about by the action of the silica on the carbonates present.

T. H. P.

Chlorine Evolution Apparatus and an Apparatus for the Electrolysis of Hydrochloric Acid for Lecture Purposes. ERWIN RUPP (*Zeit. anorg. Chem.*, 1902, 32, 359—361).—For the preparation of chlorine, the pyrolusite is placed in a flask provided with a ground-in stopper carrying a funnel and a delivery tube. The gas is washed in a wash-bottle fitted on the stand bearing the flask.

In order to save the time used to saturate the liquid with chlorine in the electrolysis of hydrochloric acid, the author has devised the following apparatus. The carbon electrodes are placed in an H-tube, the upper ends of which are attached to the tops of the ordinary U-tubes near the stopcocks. The H-tube is filled with a mixture of equal parts of concentrated hydrochloric acid and water, and the reservoir and limbs of the U-tube with saturated sodium chloride solution. An E.M.F. of 6—8 volts is used for the electrolysis.

J. McC.

Oxidation by Electrolytically Separated Fluorine. FREDERICK W. SKIRROW (*Zeit. anorg. Chem.*, 1902, 33, 25—30).—If an oxidisable substance is present in a solution in which anodic oxygen is evolved, the oxidising action of the oxygen depends on the potential. The oxidising action would therefore apparently proceed furthest by the secondary action of fluorine ions. Comparative experiments were made on the oxidation of various substances by electrolysis of solutions in hydrofluoric acid and sulphuric acid. Chrom-

ium salts and manganese salts are oxidised to a greater extent in the hydrofluoric acid solution. In the case of the manganese, there is a primary formation of manganese tetrafluoride, which is then oxidised to permanganate. In hydrofluoric acid solution, when a cobalt salt is electrolysed, the peroxide Co_2O_3 is formed, but in sulphuric acid solution there is no such formation. When a current of carbon dioxide is passed into a cooled hydrofluoric acid solution and electrolysed, no trace of percarbonic acid is formed. This favours the view of Constam and Hansen that percarbonic acid is formed on the discharge of two HCO_3' ions.

Benzene and naphthalene are oxidised by electrolysis much more quickly in hydrofluoric acid solution than in sulphuric acid solution.

J. McC.

Impurities of Compressed Oxygen, and the Part played by them in Combustions in the Calorimetric Bomb. MARCELLIN BERTHELOT (*Compt. rend.*, 1902, 135, 821—824).—The presence of moisture in the oxygen used for experiments with the calorimetric bomb is not a disadvantage, nor is that of carbon dioxide, at least, in small quantities. Owing to the formation of nitric acid when nitrogen is present, a correction has to be used if the oxygen contains this gas as an impurity. It is essential, however, that hydrogen and combustible vapours should be absent. As the pumps employed for compressing the oxygen are of necessity lubricated with grease, &c., the oxygen, before introduction into the bomb, must be freed from combustible matter by passage through a red hot copper tube. Commercial compressed oxygen, which is now largely obtained by the electrolysis of water, is found to contain only a small amount of hydrogen; by means of a special experiment, the correction necessary for this can be determined and then applied to the different experiments made with that cylinder of oxygen. It appears generally to amount to about 17 cal. per eight litres of oxygen. The quantity of carbon dioxide is always so small as to be negligible.

K. J. P. O.

Analysis of Nine Specimens of Air collected from the Galleries of a Coal Mine. NESTOR GRÉHANT (*Compt. rend.*, 1902, 135, 726—728).—The samples were taken from different galleries in the mornings from October 15th to October 23rd, 1902. The quantities of carbon dioxide varied from 1—1.8, of oxygen from 16.1—18.0, and of methane from 3.5—7.5 per cent.

J. McC.

Preparation of Sulphur Trioxide by means of the Contact Action of Iron Oxide. GEORG LUNGE and G. P. POLLITT (*Zeit. angew. Chem.*, 1902, 15, 1105—1113).—An investigation on the formation of sulphur trioxide in the presence of ferric oxide has been made as regards the influence of (1) dilution of the gases with air; (2) moisture; (3) temperature; (4) the presence of various substances; (5) the influence of quantity of contact substance necessary for the combination of the gases. The production of sulphur trioxide is equally good whether the gas contains 2 or 12 per cent. of sulphur dioxide. The mixture must be thoroughly dried

with sulphuric acid. The origin of the ferric oxide is of great importance; ferric oxide prepared from the hydroxide is by far the most active. Admixture of copper oxide is favourable to the formation of sulphur trioxide. The presence of arsenic, especially at high temperatures (above 700°), increases the activity by more than 60 per cent.; arsenic is also favourable when the iron oxide contains copper. With pure ferric oxide there is very little combination below 600° , and further, the action begins to fall off above 620° , but remains at a fairly high value until 750° . When no marked fall occurs above 620° , it is probably due to the presence of arsenic. K. J. P. O.

Theory of the Lead Chamber Process. ERNST HAAGN (*Zeit. angew. Chem.*, 1902, 15, 1135—1138. Compare Abstr., 1902, ii, 604).—Theoretical considerations are brought forward which are in opposition to the views of Riedel (Abstr., 1902, ii, 450. Compare also Lunge, *ibid.*, ii, 605). K. J. P. O.

Compounds of Sulphur and Tellurium. ALEXANDER GUTBIER and F. FLURY (*Zeit. anorg. Chem.*, 1902, 32, 272—291).—The authors have investigated the action of hydrogen sulphide on various solutions containing tellurium in the hope of isolating any impurity which may be contained in the tellurium. By the action of hydrogen sulphide on an aqueous solution of telluric acid, a precipitate is obtained containing tellurium and sulphur in the proportion $\text{Te}:\text{S}_3$; at the same time, some of the telluric acid is reduced to tellurous acid. No evidence could be obtained of the formation of thioxytelluric acid. With alkaline solutions of telluric acid, hydrogen sulphide gives a substance, the composition of which is approximately represented by $\text{Na}_2\text{TeS}_3 \cdot 2\text{H}_2\text{S}$.

When hydrogen sulphide is passed through a solution of tellurous acid, a brownish-black precipitate is obtained containing tellurium and sulphur in the proportion $\text{Te}:\text{S}_2$. Becker has shown that all but 3.69 per cent. of the sulphur can be extracted from this; using a more perfect extraction method, the authors have been able to reduce the percentage of sulphur to 1.18. When the substance is heated, the sulphur volatilises, and the authors conclude that it is not a definite chemical compound. On first passing the hydrogen sulphide through the tellurous acid solution, a red substance is obtained which might be the normal unstable disulphide, TeS_2 , but the suggestion is made that it is more probably thiotellurous acid, H_2TeS_3 or $\text{H}_2\text{TeS}_3 \cdot 2\text{H}_2\text{S}$.

An addendum contains a reply to Brauner (*Zeit. anorg. Chem.*, 1902, 32, 378). J. McC.

Colloidal Sulphides. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, 32, 292—294).—When a small amount of hydrogen sulphide is passed through a solution of tellurous acid, a pseudo-solution of tellurium disulphide is formed. It is a transparent liquid which has a blue fluorescence. After dialysis, the pure solution keeps well. By freezing, a solid hydrosol is obtained. In the same way, from a dilute solution of telluric acid, a pseudo-solution of tellurium trisulphide is formed; by transmitted light, it shows a steel-blue to violet colour. A pseudo-solution of selenium disulphide is obtained by passing

hydrogen sulphide through an aqueous solution of selenium dioxide; the solution has a yellowish-green fluorescence and is only slowly precipitated by electrolytes.

J. McC.

Boiling Point, Freezing Point, and Vapour Tension of Pure Nitrogen at Low Pressures. KARL T. FISCHER and HEINRICH ALT (*Sitzungsber. K. Akad. München*, 1902, 113—151).—For details of the preparation and manipulation of the material, reference must be made to the original.

The following constants for liquid nitrogen, containing not more than 0.3 per cent. of impurity, have been found: b. p. 76.87° abs. under 715 mm. pressure; 77.37° abs. under 760 mm. pressure; freezing point 62.52° abs., the melting pressure being 86 ± 4 mm. These values are based on the use of a constant volume hydrogen thermometer, and the absolute zero has been taken as -273.04° . The vapour tension of liquid nitrogen has been determined between its boiling and freezing points, and it is found that Ramsay and Young's rule as to the ratio of the boiling points of two substances is applicable to the case of water and liquid nitrogen. The ratio of the reduced pressures for oxygen and nitrogen at corresponding temperatures is nearly constant, but the ratio is not constant when water and liquid nitrogen are compared.

The value of dp/dT being known from the authors' work, the heat of vaporisation may be calculated with the help of Dewar's value for the specific volume of saturated nitrogen vapour (Dewar, *Abstr.*, 1902, ii, 304), and is found to be 48.9 cal. at the boiling point under 760 mm. pressure.

Hence, by van't Hoff's formula, the molecular elevation of the boiling point of liquid nitrogen may be calculated; from this molecular elevation, the effect of oxygen in raising the boiling point of nitrogen can be predicted in very close agreement with experiment.

J. C. P.

Freezing and Melting Pressure of Nitrogen. KARL T. FISCHER and HEINRICH ALT (*Sitzungsber. K. Akad. München*, 1902, 209—215. Compare the previous abstract).—In the earlier investigation, there was considerable variation in the values obtained for the melting pressure of nitrogen, and this is now attributed to the presence of a little oxygen; it is estimated that 1 per cent. of oxygen lowers the freezing pressure by 8—10 mm. Fuller investigation gives 90.0 ± 0.3 mm. as the mean value of the melting and freezing pressures of pure nitrogen.

J. C. P.

Aqueous Ammonia Solution. C. FRENZEL (*Zeit. anorg. Chem.*, 1902, 32, 319—340).—The author recapitulates the various reasons for believing that in an aqueous solution of ammonia very little of the ammonia combines with water to form a hydroxide which is practically completely ionised. The distribution-ratio, the thermochemistry, and the non-hydrolysis of the salts are in favour of this view. The author has shown (*Abstr.*, 1900, ii, 474) that in liquid ammonia the ions NH_2^- are present, and it is probable that such exist also in the aqueous

solution; this is deduced from the action of ammonia solution on ethylene oxide and from the formation of amino-mercury compounds. Attempts were made to ascertain the discharge potential of these ions by determining the decomposition curve. This, however, probably occurs at a part of the curve which cannot be found experimentally.

From a consideration of the double nature (acidic and basic) and from the comparison with organic nitrogen compounds (particularly diazo-compounds), the author is led to assume that in aqueous solution most of the ammonia is uncombined with water.

On electrolysing a solution of ammonia, nitrogen is evolved at the anode. This is due to a secondary process, oxidation by the anodic oxygen. When ammonium salt solutions are electrolysed, nitrogen is only formed if a high voltage be used, but even a low voltage gives nitrogen if free ammonia be present in the solution; consequently it is not NH_4 ions which are easily oxidised. These facts support the view that the greater part of the ammonia does not combine with the water and it is the NH_3 molecules which are oxidised. J. McC.

Orthonitric Acid and the Compounds obtained from it by Elimination of Water. HUGO ERDMANN (*Zeit. anorg. Chem.*, 1902, 32, 431—436).—*Orthonitric acid*, $\text{N}(\text{OH})_5$, crystallises in long needles which melt at -35° ; it is quite stable below -15° and boils with dissociation at $40-40.5^\circ$ under 13 mm. pressure. *Octobasic nitric acid*, $\text{O}[\text{N}(\text{OH})_4]_2$, crystallises in prisms and melts at -39° . *Tribasic nitric acid*, $\text{O}:\text{N}(\text{OH})_3$, forms rhombic crystals which melt at -34° . *Tetrabasic nitric acid*, $\text{O}[\text{NO}(\text{OH})_2]_2$, forms small crystals which melt at -65.2° ; it boils at 48° under a pressure of 15 mm. Ordinary nitric acid does not crystallise readily; it melts at -42° and boils at 21.5° under a pressure of 24 mm. J. McC.

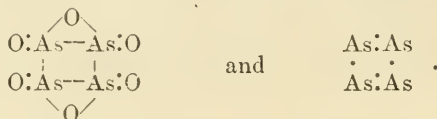
Yellow Arsenic. HUGO ERDMANN and MAX VON UNRUH (*Zeit. anorg. Chem.*, 1902, 32, 437—452).—Arsenic was distilled in an aluminium tube in a current of carbon dioxide. This tube passed directly into a side-tube of a U-tube with a bulb on the opposite limb. A rapid current of cooled carbon dioxide played on to the distilled substance just as it emerged from the hot tube. By this sudden cooling, the arsenic is deposited in the yellow modification, which was at once dissolved in carbon disulphide in the U-tube, surrounded by ice-water. The yellow modification of the arsenic can be obtained from the solution either by evaporation of the carbon disulphide or by cooling to -70° , when most of it separates from solution. The solid, yellow arsenic is extremely sensitive to all forms of light. It can be preserved for some time by keeping it at a temperature below -60° and away from the light. Even at very low temperature, it is quickly turned black by the action of light. The following amounts of yellow arsenic are soluble in 100 c.c. of carbon disulphide at the temperatures given: at 46° , 11 grams; at $18-20^\circ$, 7.5—8.0 grams; at 12° , 5.5—6.0 grams; at 0° , 3.8—4.0 grams; at -15° , 2.0—2.5 grams; and at -60° , 0.8—1.0 gram. It is less soluble in benzene and still less in ethyl acetate.

There is no tendency for the dissolved yellow arsenic to change

into the metallic modification, but the solution slowly deposits a reddish-brown modification on standing. This reddish-brown variety is not changed into the metallic form by the action of light.

The molecular weight of the yellow arsenic, determined from the rise of boiling point of carbon disulphide, corresponds with the formula As_4 . J. McC

The Constitution of Arsenious Oxide. HUGO ERDMANN (*Zeit. anorg. Chem.*, 1902, 32, 453—455).—When arsenious oxide is reduced with zinc dust in presence of carbon disulphide, a certain amount of the yellow modification of arsenic is formed. This leads the author to assume that these have similar constitutions, and those proposed are :



J. McC.

Action of Hydrogen Sulphide on Arsenious Oxide in Aqueous Solution. FRIEDRICH W. KÜSTER and GEORG DAHMER (*Zeit. anorg. Chem.*, 1902, 33, 105—107).—The quantity of hydrogen sulphide absorbed by a 0.5638*N* solution of arsenious oxide was determined and corresponds within the experimental error with the quantity requisite for the formation of arsenious sulphide and that dissolved by the water present.

In another case, a solution of arsenious oxide was saturated with hydrogen sulphide, and a current of oxygen was passed through it until no more hydrogen sulphide was removed; on acidifying with hydrochloric acid, the arsenic was completely precipitated as trisulphide. These experiments prove that, although no precipitation takes place, the arsenic is quantitatively transformed into trisulphide, which remains dissolved in the colloidal state. J. McC.

Some Constants of Carbon Disulphide. MAX VON UNRUH (*Zeit. anorg. Chem.*, 1902, 32, 407—412).—The carbon disulphide was purified by shaking with mercury and porous calcium chloride and distilling in the dark. The boiling point varies regularly with the pressure between 740 and 760 mm. For an increase of pressure of 1 mm. of mercury, the boiling point rises by 0.04144°. The sp. gr. of carbon disulphide near the boiling point varies very appreciably with the temperature and pressure. The following results have been found (the sp. gr. is referred to water at 4°):

Pressure in mm. of mercury.	Temperature.	Sp. gr.
756.6	46.10°	1.22161
758.0	46.16	1.22115
760.0	46.25	1.22093

J. McC.

Electrolysis of Fused Sodium and Potassium Hydroxides. MAX LE BLANC and JOUANNES BRODE (*Zeit. Elektrochem.*, 1902, 8, 817—822).—Two decomposition points are observed when fused potassium hydroxide is electrolysed. The first,* at 1.2 volts, corresponds with the decomposition of the dissolved water, the second, at 2.1 volts, corresponds with the liberation of potassium. These points are almost the same as those observed with sodium hydroxide (this vol., ii, 18). The main differences are that potassium hydroxide retains more water than sodium hydroxide and also absorbs oxygen much more readily, consequently oxygen is not evolved at the anode with small current densities. The nickel electrodes used are hardly acted on, although the cathode loses a little weight when very high current densities are used. Fresh potassium hydroxide, containing water, fused at 260°, and electrolysed, gives somewhat less than the theoretical quantity of hydrogen and considerably less than the theoretical quantity of oxygen; in fact, with small current densities, none at all. A comparison of sodium and potassium hydroxides, fused and electrolysed under identical conditions, shows that the latter permits considerable currents to pass at very low *E.M.F.*'s.

These facts show that potassium hydroxide absorbs oxygen (forming peroxide) much more readily than sodium hydroxide, and is therefore, in presence of air, a stronger oxidising agent. That this conclusion is not in accordance with the observed behaviour of the substances with organic compounds may be due to the larger quantity of water contained in the potassium compound. Owing to the greater oxidising power, the authors failed to obtain metallic potassium by electrolysis of the fused hydroxide.

T. E.

Synthesis of Anhydrous Hyposulphites of the Alkalis and Alkaline Earths. HENRY MOISSAN (*Compt. rend.*, 1902, 135, 647—654).—Schützenberger (*Compt. rend.*, 1869, 69, 196) assigned to the crystalline sodium hyposulphite prepared by him the formula $\text{NaHSO}_2 \cdot \text{H}_2\text{O}$. Bernthsen (*Abstr.*, 1881, 508) came to the conclusion, on the other hand, that the correct formula was NaSO_2 , or rather $\text{Na}_2\text{S}_2\text{O}_4$, a result confirmed by Nabl's analysis of the zinc salt (*Abstr.*, 1900, ii, 13). In order to throw further light on the composition of these salts, their formation by the action of sulphur dioxide on the hydrides of metals has been investigated. At -74° , liquid sulphur dioxide does not act on potassium hydride, but at -40° a violent reaction occurs. When sulphur dioxide, under reduced pressure or diluted with its own volume of hydrogen, is very slowly led over potassium hydride at the ordinary temperature, the latter is converted in the course of 50—60 hours into a colourless salt, which can be crystallised from water, free from oxygen, in slender, transparent needles. Analyses indicated the formula $\text{K}_2\text{S}_2\text{O}_4$ rather than the formula KHSO_2 ; further, an experiment carried out in such a manner that the hydrogen evolved when sulphur dioxide was led over a known weight of potassium hydride could be measured, showed that the reaction is represented by the equation $2\text{SO}_2 + 2\text{KH} = \text{K}_2\text{S}_2\text{O}_4 + \text{H}_2$. This salt reduces ammoniacal copper sulphate to copper and copper hydride; it decolorises indigo and permanganate, reduces mercuric

chloride to mercurous chloride and metallic mercury, liberates the metals immediately from silver nitrate and gold and platonic chlorides, and absorbs oxygen rapidly from the air; with hydrochloric acid, the liquid becomes yellow and deposits sulphur. Sodium hyposulphite is prepared in a similar manner from sodium hydride and sulphur dioxide; it crystallises from water in prisms of the formula $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. *Lithium hyposulphite* is only formed very slowly by this reaction at the ordinary temperature; at 50° , lithium sulphide is formed at the same time. Calcium hydride reacts very slowly with sulphur dioxide under the ordinary pressure, and is only completely converted into the *hyposulphite* under a higher pressure of 900 mm. *Strontium hyposulphite* is obtained by heating the hydride at 70° in a current of sulphur dioxide under pressure. K. J. P. O.

Colloidal Silver. II. FRANZ KÜSPERT (*Ber.*, 1902, 35, 4066—4070. Compare Abstr., 1902, ii, 656).—The results of a series of experiments are given which illustrate the influence of light and temperature on the colour of colloidal silver solutions, obtained by treating solutions of silver nitrate with formaldehyde in the presence of sodium silicate (*loc. cit.*). K. J. P. O.

Colloidal Silver and Gold. FRANZ KÜSPERT (*Ber.*, 1902, 35, 4070—4071. Compare preceding abstract).—A concentrated solution of colloidal silver can be obtained by dissolving in water the jelly prepared by adding formaldehyde to a solution of silver nitrate and then concentrating the solution on the water-bath. Under certain conditions, a colloidal silver solution can be obtained of a carmine-red colour.

By reduction of a solution of gold chloride with formaldehyde at 100° , a deep red solution of colloidal gold was formed. K. J. P. O.

Preparation of Metallic Calcium. KURT ARNDT (*Zeit. Elektrochem.*, 1902, 8, 861. Compare Borchers and Stockem, this vol., ii, 19).—An iron crucible is lined with fire-clay and dried, a layer of fluorspar is placed on the bottom and covered with calcium chloride, the cathode is an iron wire, the anode a carbon rod. The calcium chloride is fused by forming an arc between the anode and a subsidiary carbon rod held in the hand, after which the electrolysis is carried on with 20—25 amperes; on cooling, beads of calcium containing 99 per cent. of the metal are found. T. E.

The Equation Representing the Reducing Action of Calcium Carbide. FR. VON KÜGELGEN (*Zeit. Elektrochem.*, 1902, 8, 781—783).—The author maintains the accuracy of his formula (Abstr., 1901, ii, 448) against the objections of Neumann (this vol., ii, 20). T. E.

Calcium Thioaluminates and the Decomposition of Maritime Structures made of Portland Cement. II. ORAZIO REBUFFAT (*Gazzetta*, 1902, 32, ii, 158—168. Compare Abstr., 1901, ii, 385).—The author first criticises the views on the decomposition of portland and other cements put forward by Maynard in 1901 before the Buda-Pest Congress of the International Association for the Testing

of Materials of Construction. The various formulæ proposed for calcium thioaluminate are also considered.

T. H. P.

Barium-Ammonium and Baramide. MENTREL (*Compt. rend.*, 1902, 135, 740—742).—When ammonia is passed over cold barium, a red solid is formed which at -23° passes into a blue liquid, whilst at -50° a blue oil is obtained which is sparingly soluble in liquid ammonia. Below -15° , the compound, which can be represented by the formula $\text{Ba}(\text{NH}_3)_6$, is stable, but above this temperature it is converted into an amide. Barium-ammonium spontaneously inflames in the air and is violently decomposed by water. It absorbs oxygen, giving a mixture of barium dioxide and barium monoxide; with nitric oxide, it gives barium hyponitrite, and with carbon monoxide it gives barium carbonyl, $\text{Ba}(\text{CO})_2$.

When ammonia is passed over barium heated at 280° , baramide, $\text{Ba}(\text{NH}_2)_2$, is formed. When heated to a higher temperature, this decomposes into the nitride, Ba_3N_2 , which, when allowed to cool in an atmosphere of ammonia, again forms the amide, $[3\text{Ba}(\text{NH}_2)_2 = \text{Ba}_3\text{N}_2 + 4\text{NH}_3]$. A similar balanced action takes place with lithamide.

J. McC.

Behaviour of Magnesium Chloride in a Steam Boiler. WALTHER FELD (*Chem. Zeit.*, 1902, 26, 1099—1101. Compare Ost, *Abstr.*, 1902, ii, 657).—Experiments carried out in an iron boiler with water and with solutions of magnesium chloride, magnesium sulphate, and potassium, sodium, and calcium chlorides and sulphates show that in all cases hydrogen is evolved when the solution is boiled. With water and the potassium, sodium, and calcium salts, ferric oxide was deposited, but, in the presence of dissolved magnesium salt, iron passed into solution in the form of a ferrous compound. This leads to the conclusion that the water is primarily decomposed by the iron and the ferrous oxide is secondarily dissolved by the solution of magnesium salt with deposition of magnesium hydroxide. Ost's statement that "it is only necessary to have present a quantity of calcium carbonate sufficient to decompose a fourth of the magnesium salts in order to prevent entirely the dissolution of the iron" is contested, and water containing magnesium chloride must still be regarded as exercising a deteriorating influence on the walls of a steam boiler.

J. McC.

Alloys of Lead, Tin, and Bismuth. E. S. SHEPHERD (*J. Physical Chem.*, 1902, 6, 519—553).—The first part of the paper contains an exhaustive summary of the work of previous observers on the binary and the ternary alloys. The author's own experiments indicate that (1) tin crystallises pure from its alloy with lead or bismuth; (2) that bismuth crystallises with as much as 4 per cent. of lead as a solid solution; (3) that lead crystallises with about 5 per cent. of bismuth as a solid solution; (4) that there are no compounds between lead, bismuth, and tin. Microscopic examination and etching, by electrolysis in ammonium sulphide solution, confirmed the results obtained analytically regarding the existence of the solid solutions. In the ternary alloy, anomalous expansion and recalescence occur; contraction begins, in the case of

Rose's alloy, at about 43° and reaches its maximum at various temperatures; recalescence may occur at temperatures between 52° and 59° . The source of the contraction is the formation of the solid solution of lead and bismuth and occurs also in the binary alloys. The cause of this recalescence is more doubtful and is fully discussed; it is probably due to the tin, and connected with the formation of a denser allotropic form.

L. M. J.

Alloys of Copper and Magnesium. OCTAVE BOUDOUARD (*Compt. rend.*, 1902, 135, 794—796. Compare Abstr., 1901, ii, 512; 1902, ii, 501).—The melting points of a series of alloys of copper and magnesium, containing from 10 to 90 per cent. of copper, have been determined. Three maxima (550° , 585° , and 915°) and four minima (475° , 540° , 575° , and 890°) were observed; the three maxima correspond with the three compounds CuMg_2 , CuMg , and Cu_2Mg respectively. When there is less than 80 per cent. of copper present, the alloy is white. The alloy containing 10 per cent. of copper is malleable; as the proportion of copper increases, the alloy becomes brittle, and that containing 70 per cent. is so fragile that it can be broken between the fingers. There is a close analogy between these alloys and those composed of copper and aluminium.

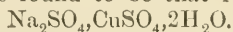
J. McC.

Oxidation of Ammoniacal Cuprous Oxide. JULIUS MEYER (*Ber.*, 1902, 35, 3952—3957).—The oxidation of ammoniacal cuprous oxide in water containing dissolved oxygen is perfectly normal and proceeds according to the equation $2\text{Cu}_2\text{O} + \text{O}_2 = 4\text{CuO}$. The abnormal results obtained by Schützenberger and Riesler (*Ber.*, 1873, 6, 678) were due to the presence of sodium sulphite, the reaction proceeding according to the equation $\text{Cu}_2\text{O} + \text{SO}_2 + \text{O}_2 = 2\text{CuO} + \text{SO}_3$.

Schützenberger's theory that half of the oxygen is employed in the production of hydrogen peroxide is untenable, since hydrogen peroxide cannot exist in the presence of cuprous compounds.

J. J. S.

Formation and Solubility Relations of Copper Sodium Sulphate. IVAN KOPPEL (*Zeit. physikal. Chem.*, 1902, 42, 1—16).—It was shown by Massol and Maldès (Abstr., 1901, ii, 594) that at temperatures somewhat above 15° the composition of solutions of copper and sodium sulphates varies with the relative quantities of the two salts, even when both are present in excess. This remarkable result led the author to seek for a double salt of copper and sodium sulphate. Such a salt would be more stable at high than at low temperatures if it contained, as would probably be the case, a smaller quantity of water than its components. Thermometric experiments indicated a formation of a double salt at about 17° , and the composition of the salt was found to be that represented by



It crystallises in deep turquoise-blue microscopic crystals. It evolves water at 160° , melts below a red heat without decomposition, but at a higher temperature evolves sulphur trioxide. Dilatometric observa-

tions indicate a transition temperature of 16.7° . The solubility of the salt in water and in solutions containing also sodium or copper sulphate was fully investigated and the solubility curves are given. It is noted that the salt appears to be identical with the natural copper sodium sulphate, cröhnite (Abstr., 1901, ii, 594). L. M. J.

Mercury Oxybromide. TH. FISCHER and H. VON WARTENBURG (*Chem. Zeit.*, 1902, 26, 966—967, 983—984).—On heating mercuric oxide and mercuric bromide under pressure at 200 — 300° , or with water at 160° , two oxybromides were obtained, $4\text{HgO}, \text{HgBr}_2$, sp. gr. 8.73, and $7\text{HgO}, 2\text{HgBr}_2$. They are readily decomposed by acids and alkalis, and by potassium bromide are converted into mercury bromide, and by aqueous ammonia into oxydimercurammonium bromide. A second modification of the oxybromide, $7\text{HgO}, 2\text{HgBr}_2$, is obtained by the action of potassium hydrogen carbonate on mercuric bromide; it has a sp. gr. 8.25, whereas that obtained directly from mercuric oxide and bromide has a sp. gr. 9.13. By the action of alkali hydroxide on mercuric bromide, an *oxybromide*, $3\text{HgO}, \text{HgBr}_2$, is formed which is not changed by treatment with an alkali hydroxide. In the preparation of hypobromous acid from bromine and mercuric oxide, there is formed an *oxybromate*, $\text{Hg}(\text{BrO}_3)_2, \text{HgO}$, and not the compound $\text{HgO}, \text{HgBr}_2$, as is generally stated. An *oxybromide*, $4\text{HgO}, \text{HgBr}_2$, is formed when a solution of mercuric bromide is left in contact with marble or magnesite. It appears that André (*Ann. Chim. Phys.*, 1884, [vi], 3, 123) did not wash the four oxybromides he obtained free from mercuric bromide. K. J. P. O.

Aluminium Chlorosulphate. ALBERT RECOURA (*Compt. rend.*, 1902, 135, 736—738).—Aluminium sulphate solution, when treated with concentrated hydrochloric acid, gives a crystalline chlorosulphate, $\text{AlSO}_4\text{Cl}, 6\text{H}_2\text{O}$, analogous to the chromium salt previously described (Abstr., 1902, ii, 563). This aluminium salt at once decomposes in water into a mixture of sulphate and chloride; in the solid condition, it is not a mixture of these, since its composition is constant; it is not produced by crystallising a mixture of the chloride and sulphate, and alcohol does not extract the chloride from it.

Ferric sulphate, treated in the same way, does not give a chlorosulphate. J. McC.

General Process for the Formation of Metallic Nitrides. ANTOINE GUNTZ (*Compt. rend.*, 1902, 135, 738—740).—By heating a mixture of 1 gram of lithium nitride and 10 grams of ferrous potassium chloride, a violent reaction takes place. On washing the product in an atmosphere of carbon dioxide, pure ferrous nitride, Fe_3N_2 , is obtained as a black, easily oxidisable powder which is soluble in dilute hydrochloric acid. Its composition is not the same as that given by Fowler (*Trans.*, 1902, 79, 285).

Lithium nitride, when heated with ferric potassium chloride or chromic chloride, gives the corresponding ferric nitride, FeN , or chromic nitride, CrN . The ferric nitride is a black substance which, when heated in the air, gives a residue of ferric oxide. The

chromic nitride may also be obtained by replacing the lithium nitride by magnesium nitride. J. McC.

Formation of Metal Oxides. I. The Behaviour of Cobalt and Nickel Solutions at the Anode. ALFRED COEHN and MORITZ GLÄSER (*Zeit. anorg. Chem.*, 1902, 33, 9—24).—It has been found that "electrostenolysis" (Abstr., 1898, ii, 365) can be carried out with cobalt but not with nickel. The anodic decomposition curves for cobalt and nickel sulphates (*N*-solutions) have been determined (*a*) in slightly alkaline solution, (*b*) in a simple aqueous solution, slightly acid on account of hydrolysis, and (*c*) in sulphuric acid solution. In slightly alkaline solution, cobalt sulphate shows an anodic formation of oxide at 1.21 volts and nickel sulphate at 1.30 volts. In the slightly acid solution, no oxide of nickel is deposited, but at 1.52 volts there is an anodic deposition of cobalt oxide. In more strongly acid solution, neither oxide is deposited. The cobalt oxide which is deposited has the formula Co_2O_3 , but it is always more or less hydrated. The thin deposits correspond with the formula $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, whilst the thicker layers correspond with $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Cobalt can be completely deposited as peroxide by electrolysing in dilute solution with a current of 0.1 ampere and 2.3 to 2.4 volts. The time taken, however, is considerable, and the process can be improved by adding potassium dichromate in order to depolarise the cathode. A complete separation of cobalt from nickel can be effected in this way, although the method is not a practical one. It may, nevertheless, be used with advantage for the detection of cobalt in nickel solutions. J. McC.

Silicides of Cobalt. PAUL LEBEAU (*Ann. Chim. Phys.*, 1902, [vii], 27, 271—277).—An account of work on the silicides Co_2Si , CoSi , and CoSi_2 , which has been already published (compare Vigouroux, Abstr., 1896, ii, 176, and Lebeau, *ibid.*, 1901, ii, 242, this vol., ii, 22). G. T. M.

Behaviour of Chromic Acid towards Caro's Reagent. A. BACH (*Ber.*, 1902, 35, 3940—3943. Compare Abstr., 1902, ii, 251).—Potassium permanganate yields, with undiluted Caro's reagent, one-third of a volume more oxygen than does hydrogen peroxide, and the author has therefore supposed that the reagent contains a higher peracid than persulphuric acid. The reagent, however, reacts with chromic acid in precisely the same manner as hydrogen peroxide, three atoms of oxygen being lost by the chromic acid for every four lost by the reagent. This reaction shows that the supposed higher peracid does not exist, but that, in the reaction with potassium permanganate, three atoms of oxygen derived from this are evolved along with five atoms derived from the reagent. The diluted reagent reacts in the normal manner with potassium permanganate, and hence probably differs in constitution from the undiluted liquid. A. H.

Extraction of Zirconium. EDGAR WEDEKIND (*Zeit. anorg. Chem.*, 1902, 33, 81—86).—Renaux's method of extracting zirconium

from zircon has been re-examined. Twenty parts of finely-powdered zircon, 12 parts of lime, and 7 parts of powdered coal were heated for seven minutes in a carbon crucible in the electric furnace with a current of 1000 amperes and 50 volts. The zirconium carbide was washed with dilute hydrochloric acid and with water, then dissolved in a mixture of hydrochloric and nitric acids. For the precipitation of the zirconium hydroxide, the best method is to add tartaric acid, then hydrogen peroxide. The reaction apparently proceeds according to the equation: $\text{ZrSiO}_4 + 2\text{CaC}_2 = \text{ZrC} + 2\text{CaO} + 2\text{CO} + \text{SiC}$.

Anhydrous zirconium chloride is obtained by heating the carbide in a current of chlorine. The reaction takes place at about 300°. The chloride dissolves in water with formation of the oxychloride, which crystallises from concentrated hydrochloric acid in colourless needles.

J. McC.

Reduction of Zirconia. EDGAR WEDEKIND (*Ber.*, 1902, 35, 3929—3932).—Zirconia is reduced by boron when heated in a carbon boat in an electric furnace, forming a mass which contains both carbon and boron, but the exact nature of which has not yet been ascertained. When the product is treated with hydrochloric acid, hydrogen containing a little boron hydride is evolved, whilst concentrated sulphuric acid yields sulphur dioxide. The substance crystallises from molten copper in small, black crystals. Silicon also reduces zirconia at a high temperature, a well-defined, crystalline silicide being produced, which is now being examined. Aluminium, applied as in the Goldschmidt process, also appears to be able to bring about the reduction of zirconia.

A. H.

Thorium Metoxide. GRÉGOIRE WYROUBOFF (*Zeit. anorg. Chem.*, 1902, 32, 376—377).—A reply to Stevens (*Abstr.*, 1902, ii, 566).

J. McC.

Silicides of Vanadium. HENRI MOISSAN and ALFRED HOLT (*Ann. Chim. Phys.*, 1902, [vii], 27, 277—288).—An account of work already published (compare *Abstr.*, 1902, ii, 610; this vol., ii, 23).

G. T. M.

Radioactive Constituent of Bismuth from Joachimsthaler Pitchblende. WILHELM MARCKWALD (*Ber.*, 1902, 35, 4239—4240).—If a few drops of a solution of stannous chloride are added to a solution of the radioactive bismuth oxychloride in hydrochloric acid, a small quantity of a dark brown precipitate is obtained after some hours. The solution is then inactive, and the precipitate, which does not exceed one ten-thousandth of the bismuth salt taken, is radioactive, and apparently only differs in this respect from tellurium.

The remainder of the paper is polemical against Giesel (this vol., ii, 20).

R. H. P.

Inorganic Colloids. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1902, 32, 347—356. Compare *Abstr.*, 1902, ii, 610, 652, 653).—A pseudo-solution of gold is obtained by reducing a dilute solution of auric chloride with hydrazine hydrate. When the reduction is made

in the cold with hydroxylamine hydrochloride, a blue hydrosol is formed, but if the dilution is so great that no reduction takes place in the cold, then a red hydrosol is formed on warming. In very dilute solution, hypophosphorous acid gives a green hydrosol with auric chloride.

When dilute solutions of silver nitrate are reduced with hydrazine hydrate, colloidal solutions of silver are obtained. According to the dilution, the solution has an olive-green to light green colour. This pseudo-solution is fairly stable and may even be concentrated by boiling without depositing silver. When slowly evaporated, it gives a mixture of a solid hydrosol and a hydrogel. Pseudo-solutions of silver could not be prepared by reduction with hydroxylamine or hypophosphorous acid.

A pseudo-solution of platinum can be obtained by using hydrazine hydrate as reducing agent, but not with hydroxylamine or hypophosphorous acid. The pseudo-solution is black to brown by transmitted light according to the concentration. It has not been possible to obtain a solid hydrosol.

A liquid hydrosol of palladium can be obtained by reduction with hydrazine hydrate.

A hydrosol of mercury is produced by reducing a mercury salt (or the oxide) with hydrazine hydrate, but this pseudo-solution is extremely unstable and difficult to prepare.

Hydroxylamine only reduces cupric salts to the cuprous state, and hydrazine gives, with cupric sulphate, a pseudo-solution of cuprous hydroxide, but when a dilute solution of cupric sulphate is reduced at 70—80° with hypophosphorous acid, a hydrosol of copper is formed which appears blue by transmitted light.

When these pseudo-solutions are shaken with animal charcoal or barium sulphate, the metal is removed from the solution. J. McC.

Cause of the Destruction of Platinum Crucibles in Phosphate Analyses. W. C. HERAEUS (*Zeit. angew. Chem.*, 1902, 15, 917—921).—The cause of the destruction of platinum crucibles in phosphate analyses has been investigated. It has been found that carbon reduces magnesium pyrophosphate at 950°, whilst reducing gases, such as hydrogen, act below 900°. The ammonia evolved on igniting ammonium magnesium phosphate acts as a strong reducing agent, and the phosphorus thus formed attacks the platinum. No general means have been found of preventing the destruction of the platinum.
K. J. P. O.

Mineralogical Chemistry.

Free Sulphur in Petroleum from Beaumont. F. C. THIELE (*Chem. Zeit.*, 1902, 26, 896—897).—Sulphur in some form or other is always found in Texas petroleum; up to the present, it has not been ascertained in what form it exists in the oil from Beaumont. Material which was deposited from the crude oil contained 63·63 per cent. of amorphous sulphur, 6·81 per cent. of crystalline sulphur and 29·56 per cent. of crude petroleum. Sulphur is also present in combination with phosphorus and arsenic. The limestone rocks in contact with the petroleum contain 1·58 per cent. of sulphur either free or combined in organic compounds.

K. J. P. O.

Bauxite Deposits of Georgia. THOMAS LEONARD WATSON (*Zeit. Kryst. Min.*, 1902, 37, 79—89; from *Amer. Geologist*, 1901, 28, 25—45).—The bauxite deposits of this region extend from Adairsville in Georgia to Alabama in the south-west. The bauxite occurs in dolomite, and is associated with gibbsite, halloysite, kaolinite, limonite, psilomelane and pyrolusite. The following mean results give the composition of the bauxite:

Analyst.	Al ₂ O ₃ .	H ₂ O.	SiO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	Total.	No. of analyses.
J. R. Gibbons	58·62	31·44	4·27	3·79	1·59	99·63	28
J. H. Hawkins	58·91	31·59	3·34	4·18	1·89	99·89	20
B. F. A. Saylor ...	61·67	29·85	4·77	2·95	0·33	99·62	4
T. L. Watson	61·92	30·61	2·68	3·54	0·82	99·57	4
„	52·94	28·40	2·83	3·78	12·29	100·24	6

In all cases, the ratio of Al₂O₃:H₂O is nearly 1:3. The structure of the bauxite is usually pisolitic; analyses of the isolated pisolites and of the matrix gave:

	Al ₂ O ₃ .	H ₂ O above 100°.	SiO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	H ₂ O at 100°.	Total.
Pisolite.	52·36	33·17	3·74	9·70	0·76	0·20	99·93
	57·26	31·69	0·99	7·63	1·89	0·39	99·85
	52·40	24·06	4·21	8·79	10·44	0·39	100·29
Matrix.	64·91	33·00	0·62	1·05	0·28	0·53	100·39
	46·92	21·68	20·46	9·80	0·28	0·34	99·48
	63·60	27·15	6·43	1·95	0·28	0·56	99·97

According to C. W. Hayes, the mode of formation of the bauxite is as follows. Beneath the limestones are beds of clay containing much pyrites: the action of sulphuric acid, produced by the oxidation of the pyrites, on the clay resulted in the formation of aluminium sulphate, which, on being transported in solution through the limestone, gave rise to calcium sulphate and aluminium hydroxide. The latter was deposited as a gelatinous precipitate from springs, and so acquired a pisolitic structure.

L. J. S.

Geikielite, Ilmenite, and Hæmatite. P. VON SUSTSCHINSKY (*Zeit. Kryst. Min.*, 1902, 37, 57—62).—*Geikielite*.—An examination of new material proves that this Ceylonese mineral is rhombohedral with [$a:c=1:1.370$]. Only one very small and imperfect crystal was observed: the massive material shows cleavages parallel to the faces of a rhombohedron ($rr'=94^{\circ}7'$) and a parting parallel to the basal plane. Sp. gr. 3.976. Analyses by F. Kaepfel gave:

TiO ₂ .	MgO.	Fe ₂ O ₃ .	FeO.	Total.
60.000	29.862	6.900	2.028	98.790
61.320	28.950	7.750	2.028	100.048

These analyses agree with the formula (Mg,Fe)O,TiO₂, but show a small excess of ferric oxide.

Ilmenite.—A description is given of a tabular crystal, with numerous faces, from Prägraten, Tyrol. Goniometric measurements gave [$a:c=1:1.38505$], and analysis showed:

TiO ₂ .	Fe ₂ O ₃ ,FeO.	Al ₂ O ₃ .	Mn ₂ O ₄ .	CaO.	MgO.	Total.
57.23	40.31	0.74	0.11	1.15	1.22	100.76

Hæmatite.—A description is given of small crystals of rhombohedral habit from Prägraten; they contain no titanium. L. J. S.

Granites of Georgia [Analyses of Felspar]. THOMAS L. WATSON (*Zeit. Kryst. Min.*, 1902, 37, 79; from *Amer. Geologist*, 1901, 27, 199—225).—Analyses of feldspars from the porphyritic granite of Columbia Co. (I) and of Coweta Co. (II) gave:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.	Sp. gr.
I.	64.64	19.64	0.37	0.67	trace	10.00	3.06	0.22	98.60	2.60
II.	64.40	18.97	0.37	0.59	trace	11.40	3.60	0.19	99.52	2.55

L. J. S.

[Augite from Easton, Pennsylvania.] F. B. PECK (*Zeit. Kryst. Min.*, 1902, 37, 86; from *Ann. N. Y. Acad. Sci.*, 1901, 13, 419—430).—In a petrological paper on the occurrence of serpentine and talc near Easton, Pennsylvania, the following analysis is given by F. H. Moffit of augite isolated from an augite-syenite:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ ,FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.
50.55	8.66	7.27	19.70	11.00	1.70	0.48	99.36

L. J. S.

Crystallography of Epidote. FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1902, 37, 1—21, 70).—The following analyses are given in a crystallographic description of epidote from various localities. I, Dark green crystals from the Rocca Rossa in the Susa valley, Piedmont. II, Pale yellowish-green crystals from Montagne des Chalanches, near Allemont in Dauphiné:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	H ₂ O.	Total.
I.	37.66	23.22	13.51	trace	23.19	0.33	1.95	99.86
II.	38.02	25.58	10.89	—	23.67	0.31	2.05	100.52

L. J. S.

The Thorite Minerals Proper (Thorite and Orangite). JOHANNES SCHILLING (*Zeit. angew. Chem.*, 1902, 15, 921—929).—A *résumé* of the previous work and analyses of these minerals is given. The following new analyses have been made by the author; I, the mean of two analyses of thorite; II, the mean of three analyses of orangite:

	SiO ₂ .	ThO ₂ .	Fe ₂ O ₃ .	UO ₂ .	Al ₂ O ₃ .	Mn ₂ O ₃ .	PbO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	17·01	50·17	7·69	9·8	0·12	0·09	0·34	1·78	0·10	0·31	0·45	12·0	99·83
II.	17·61	69·97	1·21	1·09	0·82	—	—	1·12	—	0·36	0·43	6·98	99·76

K. J. P. O.

Physiological Chemistry.

Proteid Digestion in the Stomach. KARL GLAESSNER (*Chem. Centr.*, 1902, ii, 948; from *Verh. Deut. Naturf. u. Aerzte*, 1901, ii, 48—50).—The gastric mucous membrane possesses the power of re-synthesising proteids from their decomposition products; this power is, however, limited to the proteoses among such products. The action is attributed to a synthetic ferment; it is destroyed by heat and exhibited only by the intact mucous membrane. It is, however, doubtful if the ferment in question is a rennin-like ferment.

W. D. H.

Pancreatic Secretion. HORACE M. VERNON (*J. Physiol.*, 1902, 28, 375—394, 448—473).—The ferment-liberating action of succus entericus on the pancreatic juice or on extracts of pancreas is less than that exercised by an active tryptic extract of pancreas. This activity of entero-kinase is retarded by 0·1, and stopped by 0·2, per cent. solution of sodium carbonate. Active trypsin can set the ferment free in all strengths of sodium carbonate from 0·05 to 0·6 per cent. almost as well as in neutral solutions. 0·025 per cent. solution of hydrochloric acid retards the action of entero-kinase more than that of active trypsin. Bile, in small quantities, enhances the activity of both agents, probably in virtue of its faint alkalinity. Dilute hydrochloric acid not only inhibits but destroys entero-kinase. Trypsinogen is much more stable than trypsin. Tryptic digestion of swollen fibrin takes place best at an alkalinity equal to 0·05 per cent. sodium carbonate; if the fibrin has been boiled, 0·8 per cent. of sodium carbonate is the best degree of alkalinity. Bile in amounts varying from 3 to 40 per cent. retards tryptic digestion. So also does succus entericus slightly, if the pancreatic extracts contain only free trypsin.

The ferments of the pancreas are only slowly removed by extracting agents. At first, the filtered extracts contain only the zymogens of trypsin and pancreatic rennin, but after some time (days, weeks, or months) these undergo complete conversion into their respective

enzymes. The amounts of these two ferments in successive extracts are in constant proportion. Hence it is surmised that a single insoluble pro-zymogen exists which splits into definite proportions of soluble tryptic and soluble rennetic zymogen; in time, these are transformed into the enzymes. The diastatic ferment is quite independent of these; it is more readily extracted, and, in its formation, no intermediate stage of a soluble zymogen is found. In reference to a former statement that a series of trypsins of various degrees of stability exist, it is now stated that the trypsin removed from the gland substance during the first few hours of extraction does not differ from that removed slowly after several days.

W. D. H.

The Ferment of the Pylorus. FERDINAND KLUG (*Pflüger's Archiv*, 1902, 92, 281—292).—Glaessner (Abstr., 1901, ii, 666) described a ferment which he obtained from the mucous membrane of the pylorus and also from Brunner's glands, which is a link between pepsin and trypsin. This pseudo-pepsin acts in an acid and alkaline medium and, like trypsin, forms tryptophan. The present research confirms none of these statements and the general conclusion is drawn that pseudo-pepsin does not exist.

W. D. H.

The Bile of Polar Animals. I. The Bile of the Polar Bear. II. OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1902, 36, 525—555. Compare Abstr., 1901, ii, 180).—The materials in this bile which are soluble in a mixture of alcohol and ether are divisible into two fractions by the use of acetone; the substances soluble in acetone are neutral fats and cholesterol. The principal substances insoluble in acetone are rich in phosphorus; they are termed phosphatides; one of these is lecithin, but there are others similar to those separated from the brain by Thudichum. The acid with which glycine and, to some extent, taurine are combined to form the bile acids is in part cholic acid, in part choleic acid, and a third acid termed *ursocholeic acid*, $C_{18}H_{28}O_4$ or $C_{19}H_{30}O_4$, was also separated. This is non-crystalline, is readily soluble in alcohol, ether, benzene, or chloroform; it has $\alpha_D + 16.46^\circ$ in 2.36 per cent., and 15.29° in 4.6 per cent., alcoholic solution; the taste is intensely bitter.

W. D. H.

The Behaviour of Albumoses in the Alimentary Wall and their Occurrence in the Blood. GUSTAV EMBDEN and FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1902, 3, 120—136).—The surviving trypsin-free intestinal wall, if kept in contact with the fluid to be absorbed, produces neither change in the amount of coagulable proteid, nor transformation of proteolytic products into substances which do not give the biuret reaction. The splitting of albumoses and peptone into simple substances and the "regeneration of albumin" are both denied. On the other hand, the statement is made that albumoses are absorbed as such and can be found in the blood during absorption. These are detailed as follows: the blood is boiled for from 5 to 40 minutes with potassium dihydrogen phosphate; the filtrate is concentrated and mixed with half its volume of concentrated zinc sulphate

solution containing 0.4 per cent. of sulphuric acid; the filtrate from this gives the tests for albumoses. W. D. H.

Increase in Coagulability of Blood by an Admixture with Lymph. ALMOTH E. WRIGHT (*J. Physiol.*, 1902, 28, 514—520).—The rapidity with which blood clots when allowed to come into contract with tissues like muscle is due to the admixture with lymph which thereby takes place. Lymph serum has very little influence in this direction; the effect is therefore attributable to the coagulative albuminous element which is removed when the lymph clots. The importance of these observations on the cause of the rapid coagulation which occurs when blood passes into the tissues of a wound is pointed out. W. D. H.

Permeability of the Red Corpuscles by Anions of Sodium Salts. HARTOG J. HAMBURGER and G. AD. VAN LIER (*Chem. Centr.*, 1902, ii, 1003—1004; from *Arch. Anat. Physiol.; physiol. Abth.*, 1902, 492—532).—If red corpuscles are well washed with, and then suspended in, an isotonic (4.15 per cent.) solution of dextrose, the liquid contains neither proteid nor chlorine and is completely neutral. If a neutral solution of sodium sulphate or nitrate is then added, the suspension becomes alkaline. This is more marked if the mixture has been previously shaken with carbon dioxide. If the sulphate is used, the amount of SO_4 in the fluid is lessened; if the nitrate, the amount of NO_3 is diminished; moreover, chlorine appears in the liquid. This is explained by the permeability of the corpuscles by the anions. The same holds true for a large number of other sodium salts which were tried, and the charge is more marked the more carbon dioxide the corpuscles contain. These facts form a new factor in metabolic processes. W. D. H.

Serum Globulins. ERNST FREUND and JULIUS JOACHIM (*Centr. Physiol.*, 1902, 16, 297—301).—The serum globulin of the blood is partly soluble in water (pseudo-globulin), partly insoluble, and therefore precipitable by dialysis (euglobulin). This complex character of the globulin can be shown to exist whether carbon dioxide, acetic acid, or various salts are used as precipitants. The best results are obtained by fractional precipitation with ammonium sulphate; one-third saturation of the serum with this salt precipitates the euglobulin; this precipitate, however, is again divisible into two by dialysis; the part soluble in water is called euglobulin, the insoluble portion para-euglobulin. By half saturation with ammonium sulphate, the pseudo-globulin comes down; this, however, contains a portion, insoluble in water, called para-pseudo-globulin. This fractionation of the globulin is important, because certain fractions are associated with toxins, precipitins, &c. W. D. H.

The Passage of Proteid through the Placental Walls. ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1902, 36, 498—510).—If large quantities of foreign proteid matter are injected under the skin of pregnant animals, this can be detected by the biological reaction in

the maternal, and often in the foetal, serum. If small quantities are injected, or if the proteid is given by the mouth, the reaction in the foetal serum is usually negative. Whenever the reaction is obtained with the foetal serum, it is always weak as compared with that of the mother's serum. White of egg is not discoverable at all in this way in the foetal serum. These facts are explained by supposing that the placenta acts as a kind of digestive organ, modifying the proteid which passes through into the foetal system.

W. D. H.

The Daily Nutritive Requirements of Man, especially in Relation to Proteid. R. O. NEUMANN (*Arch. Hygiene*, 1902, 45, 1—87).—Previous experiments, 307 in all, recorded in literature show that the daily 118 grams of proteid which are necessary in man, according to Voit, were exceeded in 126 cases (average 151·3 grams) and not reached in the remaining 181 cases (average 80·2 grams); the mean for the total was 109·7 grams a day. The variations recorded in the amount of fat (from 3·5—289 grams) and carbohydrate (38—908 grams a day) given are enormous. A condition of equilibrium is obtained for different individuals under the most varying conditions. The present experiments were carried out on the author's person for a period sufficiently long (746 days) to exclude numerous sources of error. This time was divided into three periods; the first and third lasted 10 months; the second, during which empirical results were controlled by experiments on metabolism, lasted 120 days. The body-weight was 70 kilos. The following table gives the numbers in each period:

	Proteid.	Fat.	Carbohydrate.	Alcohol.	Calories.
1st Period.....	69·1	90·2	242·0	45·6	2427
per kilo.....	0·99	1·3	34·5	0·65	34·7
2nd Period ...	79·5	163·0	234·0	—	2777·0
per kilo.....	1·1	2·3	33·4	—	59·7
3rd Period.....	74·0	106·0	164·2	5·3	1999·0
per kilo.....	1·0	1·5	23·4	0·07	28·5

If the amount of the nutritive constituents which were not absorbed be subtracted from these numbers, we obtain:

	Proteid.	Fat.	Carbohydrate.	Alcohol.	Calories.
1st Period.....	57·3	81·2	225·0	41·0	2199
2nd Period ...	63·5	140·0	205·0	—	2403
3rd Period.....	61·4	95·5	152·0	4·7	1766

During all three periods, although the diet was so different, equilibrium was maintained (in the third period, the weight increased by 1 kilo.), although the amount of proteid was relatively small throughout. The mean number for the total period was 74·2 grams of proteid, 117 of fat, 213 of carbohydrate, equivalent to a total of 2367 calories. The proteid figure is considerably less than that given by Voit (118), Munk (100), and Demuth (90). The amount of carbohydrate is also low (Voit's number is 500 grams per diem), so a

lessening of proteid food does not necessitate a rise in the carbohydrate of the diet. Further tables are given to show the relationship of proteid to non-nitrogenous food in each period and the relative calorific value of each nutritive constituent. Alcohol was taken in the form of beer, and yielded, in calories, more than a third of that developed by the fat in the first period. Beer, however, is expensive and unnecessary; the total daily cost of the diet varied from 7*d.* to 7½*d.*; in the first period, the beer cost nearly 3*d.* out of the 7*d.* W. D. H.

The Growth of Sucking-pigs on a Diet of Skimmed Cows' Milk. MARGARET B. WILSON (*Amer. J. Physiol.*, 1902, 8, 197—212).—Two pigs fed on skim-milk gained, in 14—16 days, 26·4 and 66·8 per cent. in weight. Two fed on the same milk *plus* 2—3 per cent. of lactose gained 49·7 and 88 per cent. Two fed in the same way, except that dextrose was substituted for the lactose, gained 73·6 and 64·4 per cent. The growth stands in constant ratio to the calories of the food. The pigs fed on plain skim-milk used 23 and 35 per cent. of the proteid in the food for tissue growth; the "lactose" pigs used 38 and 44 per cent., and the "dextrose" pigs 48 and 42 per cent. The number of calories retained in the tissues during growth is proportional to the calories of the food. All the pigs gained in fat. The percentage of calcium in their bodies diminishes with growth. There is considerable deposition of calcium in the pig, but this is proportional, not to the calcium in the food, but to the growth of the animal. W. D. H.

Does Potassium Cyanide prolong the Life of the Unfertilised Egg of the Sea-urchin? F. P. GORHAM and R. W. TOWER (*Amer. J. Physiol.*, 1902, 8, 175—182. Compare Loeb and Lewis, *Abstr.*, 1902, ii, 151).—Bacteria are killed more quickly than sea-urchins' eggs by potassium cyanide, which therefore gives the eggs a more favourable environment. If the solution is too strong, the eggs are killed also. Sterile sea-water 'prolongs' the life of the egg much longer than Loeb's most favourable potassium cyanide solutions. If unsterilised sea-water is used, the bactericidal power of the protozoa in it must not be neglected. The specific mortal processes of Loeb are purely hypothetical and without any definite experimental basis. W. D. H.

Oxygen and the 'Survival Metabolism' of Muscle. W. M. FLETCHER (*J. Physiol.*, 1902, 28, 474—498).—The loss of irritability in a surviving muscle is markedly delayed by an abundant supply of oxygen. The advent of *rigor mortis* is indefinitely delayed by the same influence, even when special means are taken to hasten it. Fatigue is delayed by oxygen, and recovery from fatigue occurs rapidly by exposing freely to oxygen. The survival discharge of carbon dioxide is increased during periods of contraction in the presence of abundant oxygen; the increase is roughly proportional to the amount of contraction. This additional yield of carbon dioxide is absent or incomplete if the muscle is in air or nitrogen. W. D. H.

Elimination of Carbon Dioxide during Activity of Muscles. JOHAN E. JOHANSSON (*Bied. Centr.*, 1902, 31, 737—738; from *Skand. Arch. Phys.*, 11, 273; *Centr. Physiol.*, 1902, 663).—The work of lifting weights with the arms increased the production of carbon dioxide by 5—6 milligrams per 1 metrekilogram up to 6500 metrekilograms in half-an-hour with a weight of 20 kilograms. With a weight of 30 kilograms, the limit is 5000 metrekilograms in half-an-hour. Within this limit, the carbon dioxide increases considerably with the duration of the contractions.

The feeling of exertion depends mainly on the duration of the contractions and on the weight, and has no relation to the amount of carbon dioxide eliminated. N. H. J. M.

Osmotic Properties of Muscle due to Fatigue. W. M. FLECHER (*Proc. Physiol. Soc.*, 1902; *J. Physiol.*, 28, xli—xlii).—Miss Cooke (*J. Physiol.*, 1898, 23, 137) found that a frog's gastrocnemius increases in weight by immersion in a 0.2 per cent. solution of sodium chloride; this is more marked if the muscle is previously fatigued, and is attributed to an increased osmotic pressure within the muscle consequent on the dissociative process of contraction. This result, however, or its opposite, can be always obtained, and depends merely on the length of immersion in the hypotonic solution; if the immersion period is prolonged to $1\frac{1}{2}$ hours, the resting muscle takes in more water than the fatigued one. If each muscle is weighed at frequent intervals, curves can be plotted out for each muscle. That for resting muscle shows a rapid gain of weight, which becomes slower later, but is well maintained up to the fifth or even the seventh hour. The fatigued muscle gains rapidly at first, but more slowly near the end of the first hour; a loss then begins and the curve descends nearly in a straight line, crossing the other. If the fatigued muscle is exposed to oxygen for a few hours before immersion in the salt solution, it behaves like a resting muscle. W. D. H.

Glycogen in the Cartilage of Mammals. EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 92, 102—103).—Glycogen can be extracted from cartilage by boiling with 36 per cent. potassium hydroxide. One hundred grams of horse's rib cartilage yielded glycogen equivalent to 0.0237 gram of dextrose. W. D. H.

Glycogen in the Skeleton. M. HÄNDEL (*Pflüger's Archiv*, 1902, 92, 104—111).—Various skeletal tissues yield to boiling 36 per cent. potassium hydroxide small quantities of glycogen. Two experiments are described, one on a dog, the other on an ox. In the dog, bone yielded 0.008, tendon 0.030, and cartilage 0.160 per cent. of glycogen. In the ox, the following were the percentages obtained: epiphyses, 0.017; diaphyses, 0.007; marrow, 0.03; tendon, 0.006; ligamentum nuchæ, 0.007; cartilage, 0.217. W. D. H.

Protagon of the Brain. W. W. LESEM and WILLIAM J. GIES (*Amer. J. Physiol.*, 1902, 8, 183—196).—The protagon of the brain is

a mixture of substances, not a chemical individual, and does not contain the bulk of the phosphorised organic substances of the brain.

W. D. H.

Saline Diuresis. ARTHUR R. CUSHNY (*J. Physiol.*, 1902, 28, 431—447).—The absorption from the renal tubules in the rabbit when the outflow is obstructed is differential, the water and chlorides returning to the blood much more readily than the sulphates, phosphates, urea, and pigment. The presence of the latter retards absorption of water by offering osmotic resistance to the absorbing force. If the absorption in the tubules under normal circumstances is differential also, a sufficient explanation of the variation in the diuretic action of different salts is obtained. The action of saline diuretics is primarily on the circulation through the kidneys, not on excretory cells.

W. D. H.

The Effect of Diminished Excretion of Sodium Chloride on the Constituents of the Urine. R. A. HATCHER and TORALD SOLLMANN (*Amer. J. Physiol.*, 1902, 8, 139—154).—The disappearance of chlorides from the urine does not produce marked changes in the other urinary constituents; neither does the administration of sodium chloride. According to V. Koranji, heart disease can be diagnosed from a high Δ/NaCl (that is, the ratio of total molecules to chloride molecules) joined with low Δ . c.c. (that is, the product of Δ and the daily amount of urine in c.c.), but the same change may be equally produced by milk diet. The addition of sodium chloride to a milk diet is recommended because it leads to a greater excretion of urine and metabolites; this is especially desirable in fever.

W. D. H.

The Mechanism of the Retention of Chlorides; a Contribution to the Theory of Urine Secretion. TORALD SOLLMANN (*Amer. J. Physiol.*, 1902, 8, 155—174).—The disappearance of chlorides from febrile urine is entirely due to the deficiency of the chloride income. It possesses no diagnostic value. The mechanism of the retention of chlorides is not explained by any physical theory and so is regarded as a "vital" process. Lessened secretion and increased reabsorption are probably both concerned in the retention. The filtration theory of urine formation is inadequate.

W. D. H.

Presence of Arsenic in Animals. GABRIEL BERTRAND (*Compt. rend.*, 1902, 135, 809—812. *Compare Abstr.*, 1902, ii, 517).—The presence of arsenic in fish from the Atlantic Ocean at a depth of 1800 metres has been proved. Arsenic appears to be, along with carbon, nitrogen, sulphur, and phosphorus, a normal constituent of protoplasm.

In medico-legal cases, the arsenic ought to be estimated quantitatively, and not merely qualitatively.

The author believes that arsenic exists in all parts of the body. In a note, ARMAND GAUTIER contests this view and states that there is no arsenic in the muscles and adipose tissue of terrestrial animals. The latter author has found arsenic in the chlorophyllous algae, both terrestrial and marine.

J. McC.

Normal Localisation of Arsenic in Certain Organs of Animals and Plants. ARMAND GAUTIER (*Compt. rend.*, 1902, 135, 833—838. Compare Abstr., 1900, ii, 152, 168, 226, 670).—In continuation of researches on the excretion of arsenic by mammals, in which it was shown that this element was always eliminated by organs of ectodermic origin, an exhaustive examination has been made of birds and fishes. In no case does arsenic appear to be present in the ova of birds or fishes. In the plumage of birds, arsenic seems to be localised in the down; it is also always found in the ornamental feathers, which are lost in moulting after the breeding season.

In the vegetable kingdom, both marine and fresh-water algæ have been investigated. Arsenic was found in considerable quantity, generally accompanying iodine; further, in fossil algæ, arsenic was present. A search for arsenic in the constituents of fresh water, which could be separated by careful filtration, showed that this element was always present. In the case of sea-water, arsenic was found in considerable amount; even in carefully filtered sea-water it could be detected. It appears to find its way into the water from the granite rocks, which contain about 0.06 mg. of arsenic per 100 grams.

K. J. P. O.

Changes in Nerve-cells after Poisoning with the Venom of the Australian Tiger Snake (*Hoplocephalus curtus*). BASIL KILVINGTON (*J. Physiol.*, 1902, 28, 426—430).—In the changes observed in the nerve-cells of rabbits after poisoning by this venom, chromatolysis is so great that ultimately all stainable substance disappears. No diffuse staining or swelling of the cells occurs. The changes are unequal in different cells, but those around the central canal of the spinal cord show the changes earliest and most markedly. Inflammatory and vascular changes are absent, and if the dose given is rapidly fatal the changes just described in the nerve-cells are not seen either.

Marinesco described very similar results as the result of abrin poisoning.

W. D. H.

Hæmolysis; the Action of Staphylolysin. HEINRICH SCHUR (*Beitr. chem. Physiol. Path.*, 1902, 3, 89—119).—Staphylolysin acts like a ferment both within and without the organism. Its activity in experiments *in vitro* increases proportionally with the time; *in vivo*, there is a limit to its activity; this is due to the excretion of the poison. In animals, the behaviour of another lysin (immune hæmolysin) is such that fermentative activity is probable. The occurrence of spontaneous aseptic hæmolysis cannot be doubted. Poisoning, with the two lysins mentioned, produces oligocythæmia, the rapid occurrence of spontaneous hæmolysis and agglutination, and the appearance of nucleated red corpuscles in the blood before anæmia sets in.

W. D. H.

Influence of Putrefaction on the Amount of Pentoses in Animal Organs. ERICH EBSTEIN (*Zeit. physiol. Chem.*, 1902, 36, 478—486).—Previous observations (with Bendix, *Zeit. allgem. Physiol.*,

1902, 2) had shown that the amount of pentoses obtainable from human organs was less than that obtained from animals. It seemed possible to explain this by supposing that the human organs cannot be obtained so fresh as those of animals. It is now shown that with lapse of time and accompanying putrefaction the pentoses do disappear; the rapidity of their disappearance is especially great in the liver.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Clostridium Pastorianum, its Morphology and its Properties as a Butyric Ferment. SERGEI WINOGRADSKY (*Centr. Bakt. Par.*, II, 1902, 9, 4354, 107—112).—*Clostridium pastorianum* is a sporogenous anaërobic organism from the soil of St. Petersburg which has the power of assimilating gaseous nitrogen and also of bringing about the butyric fermentation of certain carbohydrates. The power of producing fermentation and, to a certain extent, the course of the action depend on the nature of the nitrogenous nourishment. Dextrose, sucrose, lævulose, inulin, galactose, and dextrin are fermented in the presence of peptone, whilst only dextrose, sucrose, and inulin are attacked when ammonium sulphate is present. Lactose, arabinose, starch, gum, mannitol, dulcitol, glycerol, and calcium lactate are not attacked by the organism under any conditions. The characteristics of the butyric fermentation brought about by this organism are such that from 42—45 per cent. of the dextrose is converted into a mixture of acetic and butyric acids in varying proportions, small amounts of alcohols (ethyl, propyl, and isobutyl) are formed, and a considerable evolution of a mixture of carbon dioxide and hydrogen occurs. In an atmosphere of nitrogen, the butyric fermentation is readily set up in a culture medium quite free from nitrogenous compounds, the gaseous nitrogen being utilised to the extent of about 3 mg. per gram of sugar decomposed.

A. H.

Alcoholic Fermentation of the Must of Indian Figs with Yeast Acclimatised to Sodium Fluoride. C. ULPANI and L. SARCOLI (*Atti Real. Accad. Lincei*, 1902, [v], 11, ii, 173—178. Compare Abstr., 1902, ii, 164).—In continuation of their former investigations (*loc. cit.*), the authors find that, by means of yeasts acclimatised to solutions containing sodium fluoride, it is possible to employ the fermentation of the must of Indian figs for the commercial production of alcohol, previous sterilisation of the must being unnecessary. The yeasts made use of were grown in a series of tubes containing must with proportions of sodium fluoride increasing up to 0.25 per cent., and were then employed for pitching must also containing 0.25 per cent. of sodium fluoride. By this means, the organism which, in ordinary circumstances, induces spontaneous fermentation of the must, *Sac-*

charomyces Opuntiae, is completely suppressed, as are also secondary bacterial fermentations (lactic, mannitic, &c.), and the yield of alcohol is practically theoretical. The results obtained with such acclimatised cultivations of *S. Pastorianus II* and *S. Cerevisiae* are as follows:

	Sugar in must.	Sugar remaining.	CO ₂ (calc.).	CO ₂ (found).	Alcohol (calc.).	Alcohol (found).
<i>S. Past. II</i>	10.5552	—	5.1603	4.5989	5.3948	5.1032
<i>S. Cerevisiae</i>	10.5552	trace	5.1603	5.3692	5.3948	4.8401

T. H. P.

Action of Carbon Dioxide on the Movements of Water in Plants. P. KOSAROFF (*Bied. Centr.*, 1902, 31, 764; from *Bot. Centr.*, 1900, 83, 138—144).—Carbon dioxide reduces the consumption of water both in entire plants and in branches with or without leaves.

The withering of plants under the prolonged influence of carbon dioxide is due to diminished absorption and transpiration of water.

N. H. J. M.

Changes in Phosphorus in the Germination of Vetches. LEONID IWANOFF (*Chem. Centr.*, 1902, ii, 1001—1002; from *Ber. deut. bot. Ges.*, 20, 366—372).—Inorganic phosphates appear soon during germination, and after 30 days represent 93 per cent. of the total phosphorus. Most of the phosphates are derived from proteid phosphorus, some from the soluble phosphates, and the smallest amount from lecithin, which suffers least change during germination.

N. H. J. M.

Changes in the Proteid Phosphorus of Plants. W. ZALESKI (*Chem. Centr.*, 1902, ii, 1002; from *Ber. deut. bot. Ges.*, 20, 426—433).—In experiments with seedlings of *Lupinus angustifolius*, 10, 15, and 25 days old, it was found that organic phosphorus compounds rapidly decomposed and that, coincidentally, the inorganic phosphates increased. The phosphates are formed chiefly in the cotyledons and then migrate to the axial organs, where they accumulate. Whilst the proteid phosphorus of the cotyledons is much reduced in quantity, the other undefined phosphorus compounds migrate unchanged to the axial organs, where they are converted into phosphates.

Proteids containing phosphorus are much more stable than those which do not contain phosphorus.

The complete elimination of proteid phosphorus observed by Iwanoff (preceding abstract) is attributed to the cultivation of the seedlings having been too prolonged.

N. H. J. M.

Assimilation in Wheat. JOSEF ADORJÁN (*J. Landw.*, 1902, 50, 193—230).—The amounts of dry matter, nitrogen, ash, and phosphoric acid were determined in wheat at different periods from May to July. The greater portion of nutritive constituents are taken up

during the earlier periods of growth. Nitrogen especially is accumulated at an early stage. During the flowering phase and the period immediately preceding it, phosphoric acid is assimilated to a greater extent than nitrogen.

N. H. J. M.

Latex of Euphorbia Candelabro. ORAZIO REBUFFAT (*Gazzetta*, 1902, 32, ii, 168—172).—The fresh latex of *Euphorbia candelabro* is quite white and has a sp. gr. 0.83; when kept, it becomes coagulated to a white mass, turning yellow on drying. A very small proportion is soluble in water, and this contains saccharine matter, the calcium salt of an organic acid, and some other substances. From a litre of the latex, about 700 grams of air-dried material, insoluble in water, are obtained. When treated with organic solvents, the juice yields about 20 per cent. of insoluble gummy matter, the principal product being a white, neutral substance, *candeuphorbone*, $C_{70}H_{120}O_3$; it melts at 118—119° and is insoluble in acetic acid, water, or alkaline solutions, but soluble in neutral organic solvents and also in concentrated sulphuric acid, to which it imparts first an orange, and later a brown, colour; with bromine, it gives an *additive* compound, and when fused with potassium hydroxide it yields small quantities of an acid substance; it is not acted on by light, but, when kept for some time in a fused condition, it is transformed without loss of weight into a colourless, glassy mass which melts at 54—55°, turns yellow in the light, and, when strongly heated, decomposes, evolving an odour resembling that of gum lac. When heated with zinc dust, *candeuphorbone* gives rise to strongly fluorescent hydrocarbons of high boiling point, resembling oil of resin. From the small quantity of other substances contained in the latex, a wax-like mass melting at 155—156° was separated.

When left in a warm, damp place, the latex is rapidly attacked by moulds, and undergoes profound transformation. Extraction of this changed mass with organic solvents yields *candeuphorben*, $C_{42}H_{66}O_2$, a very stable substance, which separates in shining, flattened needles melting at 117—118°, is unchanged by light and resists the action of fused potassium hydroxide, but is dissolved by concentrated sulphuric acid.

T. H. P.

Fatty Oil contained in Apricot Kernels. KARL DIETERICH (*Chem. Centr.*, 1902, ii, 943; from *Verh. Vers. Deutsch. Naturforsch. Aerzte*, 1901, ii, 165—168).—The kernels of apricots contain 40—41 per cent. of a fatty oil which has a sp. gr. 0.915—0.9211 at 15°, and 0.9010—0.9015 at 90°; refractometer number, 65.6—67.0 at 25°, 58.0 at 40°, 52.25 at 50°; critical temperature, 46.47°; acid number, 3.53—3.60; saponification number, 193.1—215.1; Hübl's iodine number, 100—108.7; Hübl-Waller's iodine number, 107.8—108.9; it solidifies at -14° to -20°. The fatty acids melt at 4.5°, and solidify at 0°, have a sp. gr. 0.9095 at 15°, 0.8875 at 90°; refractometer number, 56.23—56.30 at 25°, 56.0 at 40°, 41.3 at 50°; critical temperature, 19.5°; Hübl's iodine number, 99.06—99.82; Hübl-Waller's iodine number, 96.64—97.90. The composition of apricot oil is very similar to that of peach or almond oil. Whilst, however, almond

oil gives a light yellow coloration with equal parts of nitric and sulphuric acids, or with fuming nitric acid, sulphuric acid and water (Biber's reaction), apricot oil yields a red coloration. It may also be distinguished from almond oil by the stability of the emulsion it forms with calcium hydroxide (Nickles' reaction). E. W. W.

Starch in Evergreen Leaves and its Relation to Carbon Assimilation during Winter. K. MIYAKE (*Bied. Centr.*, 1902, 31, 753—754; from *Bot. Mag. Tokyo*, 1900, 14, No. 158; and *Bot. Centr.*, 1901, 85, 389).—The amount of starch in evergreen leaves varies according to the species, monocotyledons generally containing less than dicotyledons, gymnospermia, and pteridophyta, and sometimes none at all. The decrease in the amount of starch reaches its minimum at the end of January; from the end of February, the amount of starch increases and is generally greater in the spring than towards the end of summer or the beginning of autumn.

In winter, the production of starch by assimilation is slow, and some of it migrates to the body of the plant.

Lidforss's statement that crystals of calcium oxalate are entirely absent in winter is not confirmed. N. H. J. M.

Feeding Horses with Peat Molasses. L. GRANDEAU and ALEKAN (*Bied. Centr.*, 1902, 31, 742—743; from *Landw. Presse*, 1902, No. 2).—In experiments with horses, it was found that the peat of peat molasses was distinctly injurious to digestion, whilst no appreciable effect was observed as regards retention by the peat of the potassium salts of the molasses.

Molasses foods not containing peat are without laxative effect when carefully employed. N. H. J. M.

Straw as Food. FRANZ LEHMANN (*Bied. Centr.*, 1902, 31, 738—740; from *Deut. landw. Presse*, 19, 445).—By heating straw chaff with twice its weight of water and 2—4 per cent. of its weight of sodium hydroxide for 6 hours under a pressure of 4—5 atmospheres, a soft product is obtained which cattle and sheep eat readily. In the case of oat straw, feeding experiments with sheep showed that 56—60 per cent. of the organic matter was digested. In another sheep fattening experiment, it was found that 1000 parts of the heated straw and 170 parts of cotton cake meal were equivalent to 1400 of clover hay.

Cows consumed large quantities of the straw fodder without injurious effects. N. H. J. M.

Cultivation of Wheat in the Experimental Fields at Grignon in 1902. PIERRE P. DENÉRAIN and C. DUPONT (*Compt. rend.*, 1902, 135, 654—657).—The yield of wheat in 1902 was the greatest since the commencement of the experiments in 1875. This is attributed to the rains in May. Irrigation of wheat in the spring is recommended when practicable.

Experiments with several varieties of wheat, with large and small grains in each case, showed that the grain of the produce was always heaviest when the heavier seed was used. N. H. J. M.

White Clover. P. PIERRE DEHÉRAIN and EM. DEMOUSSY (*Ann. Agron.*, 1902, 28, 497—522).—Inoculation experiments in which garden soil was applied to four different non-calcareous soils were only successful in one case, an acid heath soil. This soil contained the necessary microbes, but in insufficient quantity.

Liming is advantageous when a soluble phosphate or a superphosphate is applied, but is objectionable in absence of phosphates or in conjunction with phosphatic nodules.

N. H. J. M.

Importance of Chemical Investigation of Soils in their Amelioration. FERDINAND WOHLTMANN (*Bied. Centr.*, 1902, 31, 721—725; from *Ill. Landw. Zeit.*, 1899, Nos. 84 and 85).—Attention is called to the importance of the mechanical analysis of soils and a knowledge of their geological origin and the climatic conditions.

N. H. J. M.

Vegetable Soil. THÉOPHILE SCHLÖESING (*Compt. rend.*, 1902, 135, 601—605. Compare *Abstr.*, 1901, ii, 471, and 1902, ii, 422).—Two sub-soils, the one very calcareous and the other a clayey sand, were separated into constituents which settled in water in 10 seconds, 5 minutes, 1 hour, and 24 hours respectively, and the still finer particles which remained in suspension after 24 hours. The percentages of organic carbon in the different portions were found to be as follows:

Calcareous soil.					Clayey sand.				
1.	2.	3.	4.	5.	1.	2.	3.	4.	5.
0.2	0.33	1.20	3.92	2.73	0.073	0.089	0.350	3.560	2.070

In discussing the process by which organic matter becomes attached to the finest particles of the soil, the opinion is expressed that the organic and other nearly insoluble substances are first dissolved and then deposited and that their solubility is then diminished.

N. H. J. M.

Pot Experiments to Test Field Observations concerning Soil Deficiencies. BURT L. HARTWELL (*14th Ann. Rep. Rhode Island Agr. Exper. Stat.*, 1901, 274—293).—Out of four pot experiments, only one gave results agreeing with those obtained in the fields. In one case, however, the field experiment had only been for one year, and in two cases the field experiments had been made several years previously.

N. H. J. M.

Agricultural Value of Martin [Siemens] Slag. ARTHUR PETERMANN (*Ann. Agron.*, 1902, 28, 541—542; from *J. d'agr. prat.*, 1902, iii, 535).—The four slags with which the experiments were made, contained 2.19—10.80 per cent. of phosphoric acid soluble in mineral acid, 8.31—25.28 per cent. of soluble silica, and 0.19—3.70 per cent. of lime. The results of pot experiments in which wheat was grown in soil containing 0.044 per cent. of total phosphoric acid (1) with sodium nitrate and potassium sulphate, (2) as (1), with basic slag as well, and (3—6) with Martin slag in addition to nitrate and potassium sulphate,

showed that all the phosphatic manures were very effective. Two of the Martin slags gave better, and two inferior, results to those obtained with basic slag.

N. J. H. M.

Analytical Chemistry.

Gasometry by means of Victor Meyer's Vapour Density Apparatus. JULIUS MAI and M. SILBERBERG (*Ber.*, 1902, 35, 4229—4238; *Chem. Zeit.*, 1902, 26, 875).—The authors describe in detail a method of using a slightly modified form of V. Meyer's vapour density apparatus for the estimation of substances which readily evolve a gas when treated with strong sulphuric acid. The apparatus, which is partly filled with strong sulphuric acid, is fitted with a jacket through which aniline vapour is passed; the substance contained in an ignited asbestos cartridge is now dropped in, and the gas displaced by the evolution of gas in the reaction is measured over oil. The analyses of carbonates, chlorides, sulphites, and oxalates, of which the figures are given, agree well with the theoretical results.

R. H. P.

Preparation of Normal Solutions. FRIEDRICH W. KÜSTER and PH. SIEDLER (*Chem. Zeit.*, 1902, 26, 1055—1056).—It is recommended to prepare normal solutions of hydrochloric, nitric, and sulphuric acids, and also of the alkaline hydroxides, by suitably diluting a somewhat concentrated solution, the density of which is exactly known. Reference should be made to tables published by one of the authors.

L. DE K.

Proposals for a Rational Series of Sieve Numbers. ADOLF MAYER (*Zeit. anal. Chem.*, 1902, 41, 601—606).—In order to avoid the empirical and irregular increase in the dimensions of the meshes of a set of sieves, it is proposed that their linear dimensions should be made to increase in a geometrical ratio, and the series 1, 1·6, 2·5, 4, 6·3, and 10 mm. is suggested, as giving an approximate increase of 60 per cent. at each step.

M. J. S.

Estimation of Chlorine in Urine. MAURICE BERNARD (*Chem. Centr.*, 1902, ii, 827—828; from *Pharm. Zeit.*, 47, 656—657).—The urine is mixed with some sodium carbonate and potassium nitrate, evaporated to dryness, and incinerated. The ash is dissolved in a little dilute nitric acid, carefully neutralised with sodium carbonate, and the phosphoric acid removed with barium mixture. The filtrate is titrated with silver nitrate as usual.

L. DE K.

Estimation of Fluorine. WILHELM GRAF ZU LEININGEN-WESTERBURG (*Chem. Zeit.*, 1902, 26, 967—968).—The fluoride, freed, if necessary from silica, is heated at 180—200° with sulphuric acid in

a special platinum apparatus; during the heating, a current of dry air is transmitted. The hydrogen fluoride is passed through a weighed absorption tube filled with beads of Jena borosilicate glass, which it attacks with formation of silicon and boron fluorides. When no more fumes are noticed, the contents of the absorption-tube are washed with a boiling 25 per cent. solution of potassium hydroxide, then with water, alcohol, or ether, dried, and reweighed. The loss in weight multiplied by 1.313229 represents the weight of the fluorine.

L. DE K.

Titration of Dissolved Oxygen with Indigo and Hypo-sulphite Solution. A. WANGERIN and DANIEL VORLÄNDER (*Chem. Centr.*, 1902, ii, 818—819; from *Zeit. Farben u. Textilchem.*, 1902, 1, 439—442).—A modification of Schützenberger's method. A measured volume of standard 0.1 per cent. solution of indigotin sulphate is decolorised by means of a standard hyposulphite solution in a current of coal-gas; 100—200 c.c. of the water to be tested are added and the blue colour is again destroyed by careful addition of hyposulphite.

When titrating in acid solution at the ordinary temperature, the value found is just one-half of that obtained by titrating an alkaline solution at 45—50°.

L. DE K.

Analyses of Atmospheric Air. ORAZIO REBUFFAT (*Gazzetta*, 1902, 32, ii, 153—157).—The author describes modifications in the methods of air analysis, introduced for the purpose of examining the air over certain land to see whether the effluvium of a neighbouring sewage works had any injurious effect on the air. The modifications deal with the estimation of ammonia, hydrogen sulphide, and carbon dioxide, and with the aspiration and measurement of the air. The odoriferous constituents of the air, other than ammonia and hydrogen sulphide, were estimated by passing the air through paraffin oil, which was afterwards acidified with sulphuric acid and titrated with centinormal potassium permanganate solution.

T. H. P.

Volumetric Estimation of Sulphuric Acid in Sulphates. A. GAWALOWSKI (*Zeit. anal. Chem.*, 1902, 41, 614—615).—The author's method (*Abstr.*, 1888, 751) may yield incorrect results if certain precautions are neglected. There must be no ammonium salts present. Not more than 0.2 gram of substance should be taken. The standard solutions must be decinormal, not stronger. The titration must take place at the boiling temperature. Diresorcinolphthalein is superior to phenolphthalein as an indicator.

M. J. S.

Detection and Estimation of Sulphurous Acid in Wines. L. MATHIEU (*Ann. Chim. anal.*, 1902, 7, 364—367).—*Test for Sulphur Dioxide.*—A lump of marble weighing about 1 gram, 1 c.c. of hydrochloric acid, and 10 c.c. of the wine are heated in a small, round-bottomed flask and the vapour is passed through a mixture of 5 c.c. of water and 2 c.c. of iodine solution (2.54 grams of iodine and 3.5 grams of potassium iodide per litre). When about 2 or 3 c.c. have passed over, the distillate is filtered and tested for sulphuric acid.

Excess of Total Sulphur Dioxide.—To ascertain whether the sample contains more than 200 mg. of total sulphur dioxide, 10 c.c. of the sample are distilled as directed, the vapours being this time passed through a worm condenser and received into a tube containing 3.1 c.c. of the iodine solution; should the iodine be entirely reduced, there will be more than the permissible 200 mg. of sulphur dioxide (? per litre).

Excess of Free Sulphur Dioxide.—White wines may be tested by adding to 100 c.c. of the sample a few drops of starch solution and then 4.6 c.c. of iodine solution; if the blue colour still persists, the wine contains less than 30 mg. of sulphur dioxide (? per litre). White and red wines may also be tested by adding to 50 c.c. of the sample 2.3 c.c. of iodine solution, a few drops of hydrochloric acid, and 2 c.c. of 10 per cent. barium chloride solution. If the 30 mg. limit has not been exceeded, no further precipitation of barium sulphate should take place on adding more iodine.

L. DE K.

Gravimetric Estimation of Tellurium by means of Hypophosphorous Acid. ALEXANDER GUTBIER [with E. ROHN] (*Zeit. anorg. Chem.*, 1902, 32, 295—297).—An aqueous solution of telluric acid gives with hypophosphorous acid, a colloidal solution of tellurium (Abstr., 1902, ii, 653). When this solution is boiled, the tellurium is completely precipitated in a form which can easily be filtered. The method can only be used when no other salts are present which would be reduced.

J. McC.

Quantitative Separation of Tellurium from Antimony. ALEXANDER GUTBIER [and, in part, F. RESENSCHECK] (*Zeit. anorg. Chem.*, 1902, 32, 260—271. Compare Abstr., 1902, ii, 558, 652).—Muthmann and Schröder's method for the separation of tellurium and antimony does not give good results, as the tellurium is not completely precipitated under these conditions. The separation is best effected by means of hydrazine hydrate (or its hydrochloride, but not sulphate) in presence of tartaric acid. Elementary tellurium is quickly and completely precipitated (Abstr., 1901, ii, 687), and the antimony may then be precipitated as sulphide. The hydrazine may be replaced by hydroxylamine, but this is not to be recommended because it requires prolonged boiling in ammoniacal solution to effect complete reduction. Jannasch and Heimann's observation (Abstr., 1899, ii, 60) that the reduction is complete in about an hour, has not been confirmed.

J. McC.

Volumetric Estimation of Hydrazine. ROBERT STOLLÉ (*J. pr. Chem.*, 1902, [ii], 66, 332—338. Compare Abstr., 1891, 263).—Hydrazine, in hydrazine hydrate or its salts, is estimated by adding potassium or sodium hydrogen carbonate and immediately titrating with a standard iodine solution in presence of starch. As the reaction $\text{N}_2\text{H}_4 + 2\text{I}_2 = \text{N}_2 + 4\text{HI}$ finishes slowly, the coloration should persist for at least 2—4 minutes. The titration is not affected by the presence of ammonia.

As pure hydrazine sulphate is easily prepared, it is recommended as a standard for the preparation of iodine solutions.

In conjunction with methyl-orange as an indicator, hydrazine sulphate can be used for estimation of dissolved alkalis. The reaction takes place according to the equation: $2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 2\text{KOH} = (\text{N}_2\text{H}_4)_2, \text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$. The action of iodine on propylhydrazine leads to the formation of *s*-dipropylhydrazine. When iodine solution is rapidly added to benzylhydrazine, the following reaction occurs: $\text{CH}_2\text{Ph} \cdot \text{N}_2\text{H}_3 + 2\text{I}_2 = \text{CH}_2\text{PhI} + 3\text{HI} + \text{N}_2$ (compare Abstr., 1900, i, 698).

The action of iodine on phenylhydrazine in sodium hydrogen carbonate solution in an atmosphere of carbon dioxide leads to the formation of diazobenzenephénylhydrazide (compare Abstr., 1893, i, 509; 1900, i, 707) according to the equation: $2\text{N}_2\text{H}_3\text{Ph} + 2\text{I}_2 = 4\text{HI} + \text{NPh} : \text{N} : \text{NPh} \cdot \text{NH}_2$ (compare Fischer, *Ber.*, 1877, 10, 1335; Meyer, Abstr., 1887, 1042). Omission of the carbon dioxide atmosphere resulted in the formation of phenyldiazoimide and aniline.

Diazotoluenetolyhydrazide, formed by the action of iodine on tolylhydrazine, melts at 95°.

The action of iodine on benzoylhydrazine at the ordinary temperature leads to the formation of benzoic acid with evolution of nitrogen; at 0°, *s*-dibenzoylhydrazine is formed. G. Y.

Volumetric Estimation of Nitric Acid in Water. OTTO SCHMATOLLA (*Chem. Centr.*, 1902, ii, 1152—1153; from *Apoth.-Zeit.*, 17, 697—698).—A modification of Marx's process. A solution is prepared by dissolving 4—5 grams of indigotin in 80—100 grams of sulphuric acid and diluting with water to a litre. A solution of potassium nitrate containing 0.001 gram of nitric pentoxide per c.c. is also required; before use, 4 c.c. are diluted to 100 c.c. Thirty c.c. of sulphuric acid are mixed with 1 c.c. of the indigo solution, prepared by diluting the stock solution with an equal volume of water; the mixture is heated on the water-bath, and the potassium nitrate solution added at intervals of 2 or 3 minutes until the liquid is decolorised. Having thus found the titre of the indigo, which should amount to 0.12—0.32 mg. of nitric pentoxide, it may be used for the estimation of nitrates in water. Waters containing a large amount of nitrates should be suitably diluted. L. DE K.

Estimation of Phosphoric Acid by Titrating the Ammonium Phosphomolybdate Precipitate. JOSEF CÉZAR (*Chem. Centr.*, 1902, ii, 820—821; from *Bull. Assoc. belge. Chimistes*, 1902, 16, 247—253).—Nyssen's process is recommended; this consists in titrating with a standard solution of sodium hydroxide the phosphomolybdate precipitated in the cold.

One hundred parts of the yellow precipitate (containing 3.789 parts of phosphorus pentoxide) require for neutralisation 49.46 parts of sodium hydroxide. L. DE K.

Volumetric Estimation of Phosphoric Acid. DE MOLINARI (*Ann. Chim. anal.*, 1902, 7, 405—407).—*Reagents required.* A solution containing 90 grams of ammonium molybdate and a few drops of ammonia per litre, a saturated solution of ammonium nitrate, nitric

acid of sp. gr. 1.4, equivalent solutions of potassium hydroxide and sulphuric acid representing 0.001 gram of phosphoric oxide per c.c., and a solution of ammonium citrate prepared by dissolving 500 grams of citric acid in about 700 c.c. of ammonia of sp. gr. 0.92, cooling to 15°, diluting with water to sp. gr. 1.09, and then mixing with ammonia to the extent of 50 c.c. per litre.

Superphosphates. Two grams of the sample are extracted with water and the solution diluted to 250 c.c.; the residue is then treated with 100 c.c. of ammonium citrate, the extract being also diluted to 250 c.c.; 12.5 c.c. of each solution are taken for analysis. Ten c.c. of dilute nitric acid (1 : 1) and 15 c.c. of ammonium nitrate are added, and after diluting to 70 c.c. the mixture is boiled for 10 minutes; the flame is then removed and 20 c.c. of ammonium molybdate are added in two portions of 10 c.c. each. After 10 minutes, the precipitate is washed by decantation and filtration, until the washings are no longer acid. The filter and its contents are then treated with a definite volume of standard alkali, the excess of which is titrated in the usual manner with sulphuric acid and phenolphthalein.

Basic slags. Ten c.c. of the acid solution (5 grams in 500 c.c.) are mixed with ammonia until a permanent precipitate has formed; 10 c.c. of dilute nitric acid (1 : 1) and 15 c.c. of ammonium nitrate are added, and, after diluting to 70 c.c. the liquid is heated to boiling and precipitated by adding successively 5 and 10 c.c. of ammonium molybdate.

Phosphates, soluble phosphates. The same process is used as for basic slags, but in addition 10 c.c. of ammonium citrate are added and 40 c.c. of molybdate solution in two portions of 20 c.c. are used.

Mixed manures. The same process is used as for superphosphates.

L. DE K.

Estimation of Citrate-soluble Phosphoric Acid in Basic Slags by the Molybdate Method. HUGO NEUBAUER (*Zeit. angew. Chem.*, 1902, 15, 1133—1135).—The triple phosphate, obtained by Wagner's new citrate process, may contain an admixture of silica, particularly when the improved molybdate solution, containing excess of ammonium nitrate, is employed; the precipitate is, therefore, redissolved in hydrochloric acid, and the silica rendered insoluble by evaporation to dryness. After extracting the residue with hydrochloric acid, the phosphoric acid is estimated in the filtrate.

L. DE K.

Improvement in Marsh's Apparatus. ARMAND GAUTIER (*Bull. Soc. chim.*, 1902, [iii], 27, 1030—1034).—A figure of the apparatus used by the author is given in the original paper. The arsenic is first isolated as the sulphide, the latter is then dissolved in aqueous ammonium carbonate, and the dry residue from the evaporation of this solution, after oxidation with nitric acid in presence of sulphuric acid, is dissolved in water and added to the generating flask of the apparatus. The action of the acid on the zinc is started, if necessary, by the addition of platinic chloride in place of a copper salt, since the latter forms a copper arsenide which is not decomposed by acids. The issuing gas is dried by passing through a plug of dry cotton wool before being heated.

T. A. H.

Retention of Arsenic by Iron in the Marsh-Berzelius Method. CHARLES L. PARSONS and MORRIS N. STEWART (*J. Amer. Chem. Soc.*, 1902, 24, 1005—1011).—Contrary to Allen's statement (*J. Soc. Chem. Ind.*, 1902, 21, 94) that a trace of iron added to the liquid to be tested for arsenic insures a more regular evolution of hydrogen and the formation of uniformly deposited mirrors in the Marsh-Berzelius apparatus, the authors state that the presence of iron either in the zinc employed or in the solution is fatal to the correct determination of arsenic. If only a qualitative test is required, a trace of iron does not interfere. The missing arsenic is found along with iron in the residue obtained from the liquid when it is evaporated to dryness with nitric acid. L. DE K.

Simplified Elementary Analysis. MAXIMILIANO DENNSTEDT (*Zeit. anal. Chem.*, 1902, 41, 525—539).—The combustion is made in a stream of oxygen in a tube containing platinised quartz fragments. No furnace is required, the tube being laid in a trough and supported near its ends by two simple stands, whilst the heat is supplied by several Bunsen or Teclu burners. Two lateral troughs support short heat reflectors; the stands, troughs, and reflectors are made of sheet-iron, the last two being lined with asbestos (see Fritzsche, *Annalen*, 1897, 294, 83). The substance is always introduced in a porcelain boat. The arrangements for the introduction of purified air and oxygen are of the usual type, calcium chloride and soda-lime being employed as absorbents for the products of combustion. At the end of the system is placed a wash-bottle containing dilute palladium chloride solution, which serves as a gas regulator and is blackened when unburnt substance passes through the platinised quartz. The combustion is allowed to take 2—3 hours, but requires attention only about every quarter of an hour. If the substance contains nitrogen, three boats containing lead dioxide are introduced between the platinised quartz and the calcium chloride tube but are not heated until the whole of the substance is burnt, as the absorption of the oxides of nitrogen is only complete in the presence of moisture. Sulphur, chlorine, and bromine are also absorbed by the lead dioxide, and can then be estimated by the ordinary methods. Iodine is not arrested, but can be taken up by finely divided (molecular) silver. A similar arrangement is used for the Dumas nitrogen estimation, the tube is then charged with coarse copper oxide, the substance is mixed with finer oxide, and carbon dioxide is supplied by heating sodium hydrogen carbonate. With the exception of carbon disulphide, no organic substance has been met with which could not be analysed by this method. M. J. S.

Estimation of Carbon Monoxide and Carbon Dioxide in Vitiated Air. FERDINAND JEAN (*Compt. rend.*, 1902, 135, 746—748).—In the apparatus devised, the suspected air is drawn first through a wash-bottle containing 50 c.c. of $N/1000$ palladious chloride solution (or an ammoniacal solution of silver nitrate). Eight to 10 c.c. of carbon monoxide produce an appreciable black deposit, which serves

as a measure of the quantity of carbon monoxide in the air. After passing through this solution, the air is drawn through a wash-bottle containing 5 c.c. of $N/2$ potassium hydroxide and 45 c.c. of water coloured with Blue, C4B. In order to change the colour of the indicator, 88 c.c. of carbon dioxide are required, and from the volume of air passed through until this change takes place the amount of carbon dioxide present in the air can be found. The air finally passes through a wash-bottle containing sulphuric acid, which becomes yellowish or brown if hydrocarbons or other volatile organic compounds are present in the air. The numbers given apply to air at 18° .
J. McC.

Analysis of Carborundum (Silicon Carbide). ALBERTO GOETZL (*Chem. Zeit.*, 1902, 26, 967).—The compound is heated with excess of lead oxide out of contact with air. If more metallic lead is obtained than is required by theory, the sample contains excess of carbon (graphite), but if less is obtained, it points to admixture of sandy matter. This analysis may be checked by absorbing and weighing the carbon dioxide formed during the combustion.
L. DE K.

Estimation of Free and Combined Alkali in Sulphite Liquors. R. SCHWARTZ (*Chem. Zeit.*, 1902, 26, 897).—The alkali, in combination with sulphurous acid, is estimated by titrating the sulphur dioxide with $N/10$ iodine solution, each c.c. of which represents 0.0031 gram of sodium oxide.

After destroying the blue colour by careful addition of solution of sodium thiosulphate, the free alkali is titrated with $N/5$ sulphuric acid, each c.c. of which represents 0.0062 gram of sodium oxide. The total amount of sodium oxide may be found by evaporating a portion of the liquid with sulphuric acid and weighing the residual sodium sulphate. From these data the sodium existing as sulphite, sulphate, and uncombined alkali may be calculated.
L. DE K.

Simplified Estimation of Potassium. B. SJOLLEMA (*Chem. Zeit.*, 1902, 26, 1014—1015).—The troublesome removal of sulphuric acid in manures containing potassium salts, such as kainite, may be simplified by using a sludge of freshly precipitated barium carbonate instead of barium chloride. The mixture should be boiled for half an hour, and if the substance contains but little magnesium chloride some of this salt should be added. A filtrate free from sulphates is obtained which may then be treated with platinum chloride and a few drops of hydrochloric acid.
L. DE K.

Analysis of Bleaching Powder. LUDWIG VANINO (*Zeit. anal. Chem.*, 1902, 41, 539—541).—A table giving the weight of 1 c.c. of chlorine at temperatures from 10° to 30° and for every millimetre of pressure from 700 to 770 mm. For the gasometric evaluation of bleaching powder, Scheibler's calcimeter can generally be used with sufficiently satisfactory results.
M. J. S.

Estimation of Calcium Sulphide in Bone Charcoal. ADELBERT RÖSSING (*Zeit. anal. Chem.*, 1902, 41, 610—614).—When large amounts of calcium sulphide are present, oxidation with potassium chlorate and hydrochloric acid, or even with bromine water, is attended with escape of hydrogen sulphide and consequent low results; but if the substance is treated successively with an alkali hydroxide and excess of bromine and subsequently boiled and acidified, this error is completely avoided.

M. J. S.

Estimation of Zinc as Sulphide. A. TIHEL (*Zeit. anorg. Chem.*, 1902, 33, 1—8).—Precipitated zinc sulphide is difficult to filter, but if zinc solution is treated successively with ammonium acetate and hydrogen sulphide solution and the mixture containing excess of these reagents boiled in a round-bottomed flask for two minutes, the zinc sulphide readily separates as a flocculent precipitate. After settling, the clear liquid is decanted through a filter and the precipitate washed by decantation with hot water containing hydrogen sulphide. The precipitate is transferred with as little water as possible to a 50 c.c., Jena-glass, conical flask, and in this vessel, together with the filter ash, it is dried by heating first on the water-bath in a current of air and then in a small asbestos furnace in a current of hydrogen sulphide, the hydrogen sulphide being finally displaced by a current of hydrogen. This is repeated until the weight of the flask is constant.

The author recommends heating sulphides (of zinc, manganese, iron, lead, and copper) in a current of hydrogen sulphide rather than with sulphur in a current of hydrogen.

J. McC.

Estimation of Zinc by Cohn's Method. LUCIEN L. DE KONINCK and M. GRANDRY (*Chem. Centr.*, 1902, ii, 822—823; from *Bull. Assoc. belge. Chimistes*, 16, 234—339).—Cohn's process (*Abstr.*, 1902, ii, 50) is recommended. The reagent is, however, best made by dissolving 1 mol. of mercuric thiocyanate in a solution containing 2 mols. of potassium thiocyanate. This is standardised by means of silver nitrate, the excess of which is then titrated with potassium thiocyanate (Volhard's process). It is not advisable to prepare the reagent by mixing mercuric chloride and potassium thiocyanate, as suggested by Cohn, because this introduces chlorine.

L. DE K.

Detection of Cadmium in Zinc Ores. R. BIEWEND (*Chem. Centr.*, 1902, ii, 821—822; from *Berg.-Hüttenm. Zeit.*, 61, 401—403).—The behaviour of cadmium, when heated on charcoal with the blowpipe, is well known and admits of the detection of very minute traces. The author has found that this metal may be also readily detected in zinc ores by heating 0.1—0.5 gram of the sample in a narrow glass tube with the addition of charcoal, potassium oxalate, spathic iron ore, or aluminium. Beyond a zinc deposit will then be noticed a deposit either of metallic cadmium or its oxide, which may be converted into the characteristic sulphide by igniting and exposing to sulphur vapour. Or it may be heated in contact with air and thus completely converted into the characteristic brown oxide.

L. DE K.

Electrolysis of Copper Sulphate as a Basis for Acidimetry. WILHELM LANGE (*Zeit. anal. Chem.*, 1902, 41, 609—610).—The electrolysis of pure copper sulphate always yields a spongy metal which is not well adapted for weighing. If nitric acid is added, the copper is obtained in the crystalline form, and the nitric acid is reduced quantitatively to ammonia. The proportion of nitric acid must be between 10 and 30 per cent. of the weight of the copper. Accurate results are obtained by determining the relation between the alkali and the $N/10$ nitric acid before and after electrolysis.

M. J. S.

Iodometric Estimation of Copper as Cuprous Xanthate. ERWIN RUPP and L. KRAUSS (*Ber.*, 1902, 35, 4157—4160).—Copper may be estimated by precipitating copper salts with a solution of potassium xanthate containing sodium hydrogen carbonate and estimating the excess of potassium xanthate in an aliquot part of the filtrate by titration with iodine in the presence of sodium hydrogen carbonate and starch, the reaction being $2\text{OEt}\cdot\text{CS}_2\text{K} + \text{I}_2 = 2\text{KI} + \text{S}_2(\text{CS}\cdot\text{OEt})_2$. The potassium xanthate solution is previously standardised against iodine, and rapidly changes in titre. The cupric salt, which is first formed in the reaction, $2(\text{OEt}\cdot\text{CS}\cdot\text{S})_2\text{Cu} = (\text{OEt}\cdot\text{CSS})_2\text{Cu}_2 + \text{S}_2(\text{CS}\cdot\text{OEt})_2$, decomposes into ethyl oxysulphocarbonate and the insoluble cuprous salt; the latter is filtered off. The process can be carried out in the presence of acetic acid, and yields excellent results.

A. H.

Cause of the Loss of Mercury in the Decomposition of Organic Substances by Fresenius and Babo's Method, and in the Purification of Mercury Sulphide. CARLO PIERPAOLI (*Chem. Centr.*, 1902, ii, 73, 914; from *Boll. Chim. Farm.*, 41, 561—568).—Experiments with horse-flesh, to which mercuric chloride had been added, showed that no loss of mercury takes place during the evaporation on the water-bath. The mercury sulphide obtained from the solution after the decomposition of the organic matter is completed must be thoroughly freed from chlorides, otherwise further treatment of the sulphide with sulphuric and nitric acids at 170° causes some loss of mercury. The purification of the mercury sulphide is more safely attained by the use of nitro-hydrochloric acid. Fresenius-Babo's method for the destruction of organic substances was found to give better results than the processes of Gautier, Denigès, and others.

W. P. S.

Testing of Cerium Oxalicum Medicinale. C. R. БОНН (*Chem. Centr.*, 1902, ii, 980—981; from *Pharm. Zeit.*, 47, 737—739. Compare Abstr., 1902, ii, 455).—*Cerium oxalicum medicinale*, a white, granular powder, is not affected by exposure to the air, and is soluble in acids but not in water or alcohol. In order to test for cerium, 0.1—0.2 gram is dissolved in about 10 c.c. of dilute nitric acid (1:5), and hydrogen peroxide and ammonia are added to the warm solution until it is alkaline. The brown precipitate which is formed resembles

a hydroxide and dissolves in hydrochloric acid with liberation of chlorine. Oxalic acid is detected by boiling about 1 gram of the salt with 20 c.c. of sodium or potassium hydroxide solution, acidifying the solution with acetic acid and finally precipitating with calcium chloride; the quantity of the acid is determined by Stolba's volumetric method. In another portion of the alkaline filtrate, aluminium is tested for by means of ammonium chloride, and in a second portion zinc and iron are precipitated by hydrogen sulphide. The presence of carbonates is shown by the evolution of carbon dioxide when the powder is treated with acid, and the heavy metals are precipitated in the acid solution by hydrogen sulphide. Lanthanum and didymium are recognised by the brown colour of the oxide formed by ignition of the oxalate. If the oxide forms a clear solution when heated with concentrated nitric acid on the water-bath, the salt may be taken to contain not more than 45 per cent. of cerium, but if a residue is left, other than silica, the percentage is higher. When the oxalate contains lanthanum and didymium, the cerium is estimated by Bunsen's or by von Knorre's volumetric method; the quantity of didymium is determined by Vierordt's spectroscopic method, and the lanthanum estimated by difference.

E. W. W.

Estimation of Manganese in Rocks. MAX DITTRICH (*Ber.*, 1902, 35, 4072—4073).—Manganese in very small quantities (0.1–0.2 per cent.) is very often found in rocks together with a very much larger quantity of iron. It is entirely precipitated from the solution of the rock in the form of hydrated peroxide, together with iron, aluminium, and titanate acid, by adding ammonia and ammonium chloride together with hydrogen peroxide. This precipitate is fused with sodium hydroxide and hydrogen peroxide added to the aqueous extract, when the iron and the whole of the manganese are thrown down leaving the alumina in solution. The manganese is obtained from the solution of the iron and manganese by warming the acidified solution with ammonium persulphate for some hours; the precipitate of manganese contains a small quantity of iron which can be separated by precipitating the iron by means of ammonia in the presence of hydroxylamine; under these conditions, only the iron is precipitated.

K. J. P. O.

Separation of Manganese from Cobalt and Nickel. M. EMM. Pozzi-Escot (*Ann. Chim. anal.*, 1902, 7, 376).—The solution, which must contain a large excess of ammonium salts and ammonia, is mixed with hydrogen peroxide or ammonium persulphate, which completely precipitates the manganese as hydrated peroxide and leaves the cobalt and nickel in solution; if but little nickel and much cobalt are present, the liquid shows the red colour of a percobaltic salt.

The manganese precipitate is then converted by ignition into manganoso-manganic oxide.

L. DE K.

Standardisation of Permanganate with an Oxalate. C. RÜST (*Zeit. anal. Chem.*, 1902, 41, 606—608).—Manganese oxalate, dried over sulphuric acid, always contains $2\text{H}_2\text{O}$, and being non-hygroscopic serves as a convenient salt for standardising permanganate;

it is prepared by boiling pure manganous carbonate with a small excess of oxalic acid and washing on the filter pump. The method is free from the disadvantages attending the use of lead oxalate as advocated by Stolba.

M. J. S.

Estimation of Iron in Natural Waters. LUDWIG W. WINKLER (*Zeit. anal. Chem.*, 1902, 41, 550—552).—The iron existing in solution as ferrous hydrogen carbonate in natural waters can be very conveniently estimated colorimetrically by treatment with ammonium sulphide. For quantities ranging from 0.3 to 1.5 mg. of iron per litre, 100 c.c. of the water are treated in a cylinder with 5 c.c. of hydrogen sulphide solution and 1 or 2 drops of ammonia. For a standard of comparison, a similar mixture is made with distilled water, and a solution of ferrous ammonium sulphate containing 0.7 gram per litre is added until the depth of colour is approximately the same. Since the tint of the latter mixture will incline to a bluish-black whilst that of the former will be brown, the standard mixture should be decolorised by acidifying with hydrochloric acid and again rendered alkaline with ammonia. If necessary, more iron solution can then be added, and the equality of colour should finally be confirmed by acidifying both mixtures and again adding ammonia. Ferric iron, which gives a far less sensitive reaction, may be reduced by warming with acidified hydrogen sulphide before adding ammonia.

M. J. S.

Stannous Chloride. M. DE JONG (*Zeit. anal. Chem.*, 1902, 41, 596—601).—Stannous chloride is one of the few inorganic compounds soluble in ether. The ethereal solution gives a brownish-red ring when added to hydrochloric acid containing 1/50 mg. of arsenious acid. This reaction can be employed in the presence of sulphuric acid and bismuth, which is not the case with Bettendorf's process. An acidified solution of stannous chloride dissolves lead sulphate freely, converting it into lead chloride.

M. J. S.

Sulphuric Acid as Solvent for Alloys of Tin. H. NISSENSON and F. CROTOGINO (*Chem. Zeit.*, 1902, 26, 984—985).—The process is more particularly applicable to alloys containing much tin and antimony with a small quantity of copper. 0.5 gram of the alloy is heated with 7 c.c. of strong sulphuric acid, when, in the absence of lead, a clear solution is obtained which, on being diluted, completely deposits the oxides of tin and antimony; these, after ignition, may be weighed together. Another portion of the solution in sulphuric acid is mixed with dilute hydrochloric acid, and the antimony is precipitated by means of iron wire; as it may contain copper, it must be separated from this in the usual manner. Copper, iron, cadmium, &c., will be found in the filtrate from the oxides of tin and antimony. If lead is present, the sulphuric acid solution is mixed with a large excess of solution of ammonium oxalate, and the lead sulphate is collected. The filtrate contains the tin and any other metals, which are then separated as usual.

L. DE K.

Estimation of Tin and its Separation from Antimony. CH. RATNER (*Chem. Zeit.*, 1902, 26, 873—874).—A modification of Rössing's process (*Abstr.*, 1902, ii, 230). If the quantity of tin does not exceed 0.5 gram in 500—600 c.c. of liquid, there is no need for a further purification of the antimony sulphide precipitate. To recover the tin from the oxalic acid solution, the author proceeds as follows.

After expelling the hydrogen sulphide by boiling, a piece of zinc is introduced and the boiling continued until the liquid is free from tin. The liquid is then decanted through a filter, and the zinc and metallic particles are rinsed into a small beaker. Nitric acid is added to dissolve the excess of zinc and convert the tin into metastannic acid, which is then ignited and weighed as oxide. L. DE K.

Quantitative Separation of Iron from Zirconium. Zirconium Peroxide. HANS GEISOW and P. HORKHEIMER (*Zeit. anorg. Chem.*, 1902, 32, 372—375. Compare Gutbier and Hüller, *Abstr.*, 1902, ii, 701).—Zirconium salt solutions are not precipitated by sodium hydroxide in presence of hydrogen peroxide. For the separation of the two metals, the solution must be dilute; to it is added 3 to 4 times its volume of ordinary hydrogen peroxide, and then 10 to 12 times as much alkali as is required for the complete precipitation of the iron. The iron is completely precipitated and carries down no zirconium.

Good results can also be obtained by precipitating with a solution of sodium dioxide in ice water.

Zirconium peroxide can be deposited only by using concentrated solutions and 30 per cent. hydrogen peroxide. J. McC.

Separation of Thorium from Cerium, Lanthanum, and Didymium, and its Application to the Analysis of Monazite. FLOYD J. METZGER (*J. Amer. Chem. Soc.*, 1902, 24, 901—917).—*First Method.*—The oxalates of the rare earths, obtained in the usual way, are boiled with strong aqueous potassium hydroxide. The mixed hydroxides are washed, dissolved in dilute hydrochloric acid, and evaporated to dryness. The residue is dissolved in water and boiled with 25—30 c.c. of a saturated solution of sodium thiosulphate. The precipitate is collected on a filter and washed. The filtrate is precipitated with excess of ammonia and the precipitate, after washing, is dissolved in hydrochloric acid and evaporated to dryness; the residue is then dissolved in water, again boiled with sodium thiosulphate, and the precipitate thus obtained is collected on the filter containing the main precipitate. This insoluble product is then boiled with aqueous potassium hydroxide, and, after being washed, is dissolved in dilute nitric acid and evaporated to dryness. The residue is dissolved in water and precipitated with oxalic acid, and the washed precipitate then rinsed into a beaker containing 100 c.c. of a saturated solution of ammonium oxalate, and, after heating on the water-bath for an hour and a half, is diluted to 300 c.c. and left overnight. The filtrate is precipitated with excess of ammonia, the precipitate is collected, and redissolved in nitric acid. After expelling the acid by evaporation, the residue is dissolved in water and precipitated with

oxalic acid. The thorium oxalate is then ignited and weighed as dioxide.

Second Method.—The oxalates are treated with potassium hydroxide as before, dissolved in dilute nitric acid, and evaporated to dryness. The residue is dissolved in 50 c.c. of water, and then diluted with water and alcohol to 200 c.c.; the alcohol should amount to 40 per cent. of the whole. 20—25 c.c. of a 1 per cent. solution of fumaric acid are added and the mixture boiled. The precipitate is washed with hot 40 per cent. alcohol, and dissolved in dilute hydrochloric acid, which is then evaporated to dryness. The residue, dissolved in 50 c.c. of water, is then diluted to 150 c.c. with alcohol and water so as to produce a 40 per cent. alcoholic solution; 10 c.c. of fumaric acid are added, and the liquid boiled. The precipitate is collected, washed, ignited while moist, and finally weighed as dioxide. In this process, it is not necessary to remove any metals precipitable by hydrogen sulphide before precipitating the oxalates. L. DE K.

Reduction of Vanadic Acid by the Action of Hydrochloric Acid. FRANK A. GOOCH and L. B. STOOKEY (*Amer. J. Sci.*, 1902, [iv], 14, 369—376).—Bunsen and Mohr proposed to estimate vanadic acid by boiling it with strong hydrochloric acid and estimating the liberated chlorine iodometrically. Gibbs got fairly satisfactory results with this process, but Milch, Rosenheim, and Holverscheit failed to get anything like the calculated quantity.

The authors now state that the reduction is fairly complete, but that it is necessary to boil repeatedly to dryness with strong acid, or else to saturate the liquid again with hydrogen chloride during the digestion. When the liquid, saturated with acid, remains clear blue when cooled by ice, the reduction may be taken to be complete. There is often a slight mechanical loss of evolved chlorine, and the residual liquid may be therefore titrated with permanganate. L. DE K.

Iodometric Estimation of Bismuth as Chromate. ERWIN RUPP and G. SCHAUMANN (*Zeit. anorg. Chem.*, 1902, 32, 362—365).—The solution containing the bismuth should contain as little acid as possible. A given bulk is added to a known volume of standard potassium chromate solution (about 5 per cent.) and the mixture well shaken. The liquid is made up to a definite volume and the precipitate filtered. Potassium iodide is added to a known volume of the filtrate and the free iodine estimated by sodium thiosulphate. From the amount of chromate used in the formation of the bismuthyl chromate, $(\text{BiO})_2\text{Cr}_2\text{O}_7$, the quantity of bismuth can be calculated.

J. McC.

Assay of Gutta-percha. ED. MARCKWALD and FRITZ FRANK (*Zeit. angew. Chem.*, 1902, 1029—1032).—Two grams of the dried sample are dissolved in 15 c.c. of chloroform and slowly poured into 75 c.c. of acetone contained in a weighed Erlenmeyer flask with a narrow neck. The gutta-percha is precipitated as a voluminous, porous cake, whilst the liquid contains resinous and suspended matters. The

solution is transferred to a weighed flask, and after washing the deposit with acetone, which is added to the main liquid, it is dried at 100° and weighed. If necessary, the liquid is filtered to separate the insoluble matters; if it is desired to weigh these impurities directly, a weighed filter should be used. The filtrate is then evaporated and the residual resin dried and weighed. Any gutta-percha on the filter may be recovered by dissolving in hot toluene and evaporating. The sample may also be tested by dissolving in chloroform and precipitating with alcohol (not to be recommended), or ether, and good results are also obtained by extracting with boiling light petroleum, which, on cooling, deposits the gutta-percha, which is then freed from resin by treatment with chloroform and ether. The authors, however, prefer the chloroform-acetone method.

L. DE K.

Estimation of Prussian Blue in Spent Gas-purifying Material. R. SCHWARTZ (*Chem. Zeit.*, 1902, 26, 874—875).—The apparatus consists of a wide-mouthed bottle fitted with a doubly-perforated, india-rubber cork. Through one of the openings passes a rectangularly bent tube reaching to the bottom of the flask and having its lower end covered with brass or phosphor-bronze gauze; the other end is fitted by means of a piece of india-rubber and a screw-clamp to a bent tube leading to a measuring flask. Through the other opening of the cork passes a short bent tube connected with the tube from a reservoir placed at a considerable height and containing distilled water.

The bottom of the bottle is covered with a layer of sand, $1\frac{1}{2}$ to 2 cm. thick, on which is placed the material to be tested, and a sufficiency of aqueous sodium hydroxide. After warming for some time, the screw-clamp is loosened, when the pressure of the column of water drives the perfectly clear solution into the measuring flask.

The ferrocyanide is then estimated as usual by precipitating the acidified solution with ferric chloride, finally igniting the blue precipitate, and weighing as ferric oxide.

L. DE K.

Estimation of Prussian Blue in Spent Gas-purifying Material. H. LÜHRIG (*Chem. Zeit.*, 1902, 26, 1039—1041).—The processes based on the estimation of iron in the alkaline extract of the sample, or in the blue precipitate obtained by precipitating the acidified solution with ferric chloride, give results decidedly in excess of those obtained by Knublauch's titration process with copper sulphate; the results, however, agree well with those obtained by estimating the nitrogen in the prussian blue precipitate.

At present it is still somewhat difficult to say whether Knublauch's process or the other methods should be used for the evaluation of spent iron oxide.

L. DE K.

Volumetric Estimation of Thymol. EMIL ZDAREK (*Zeit. anal. Chem.*, 1902, 41, 553).—The author recognises Vortmann's claim for priority for the method of estimating thymol by bromine absorption (*Abstr.*, 1902, ii, 536).

M. J. S.

Separation of Maltose and Lactose. CHARLES I. BOYDEN (*J. Amer. Chem. Soc.*, 1902, 24, 993—995).—The copper-reducing power of a solution containing about 0.5 per cent. of the mixed sugars is determined. Another portion of the liquid is mixed with 1 per cent. of Pasteur's mixture and well sterilised. It is then inoculated with a pure culture of *Saccharomyces anomolus* and incubated for two or three weeks at about 30°; the culture is grown in agar and transferred to Pasteur's mixture prior to its use. The liquid is then passed through a bacteria filter, and the copper-reducing power again determined. In this case, the reduction is due only to lactose, which has remained unchanged, whilst the maltose has been completely fermented.

L. DE K.

A New Reaction for the Detection of Acetoacetic Acid in Diabetic Urine. E. RIEGLER (*Chem. Centr.*, 1902, ii, 73, 846—847; from *Bull. Soc. Sci. Bucarest*, 11, 290—292).—Urine containing acetoacetic acid, when mixed with 20 to 30 drops of concentrated sulphuric acid and 5 c.c. of 6 per cent. iodic acid solution, gives a red coloration. The colour is insoluble in chloroform and is not due to free iodine. Acetone, sugars, leucine, and tyrosine do not give the coloration, which disappears on evaporation. When 50 c.c. of the urine are shaken with 2 c.c. of sulphuric acid and 5 to 10 c.c. of iodic acid solution, and the mixture left for some time, irritating vapours are given off which attack the eyes and nose.

W. P. S.

Polarimetric Estimation of Tartaric Acid in Commercial Products. EDGAR B. KENRICK and FRANK B. KENRICK (*J. Amer. Chem. Soc.*, 1902, 24, 928—944).—The tartaric acid is examined polarimetrically in ammoniacal solution, but the free ammonia should not exceed 2 c.c. in 50 c.c. of liquid. In the absence of substances which interfere, and using a 20 cm. tube, the number of grams of acid in the material taken is given by the formula $y = 0.00519 x$, where x is the rotation in minutes.

Calcium and magnesium salts must be removed by dissolving the sample in water containing a little hydrochloric acid, and precipitating by cautious addition of ammonia and sodium phosphate. The effect of iron and aluminium compounds may be entirely annulled by adding citric acid, ammonia, and ammonium molybdate, also magnesium sulphate if much phosphoric acid is present. Sugar, if present, must be estimated and allowance made for its rotatory power.

A long list is given of substances which interfere more or less, and also many test-analyses. For working details, the original article should be consulted.

L. DE K.

Detection of Citric Acid in Wine. JOSEF SCHINDLER (*Chem. Centr.*, 1902, ii, 1016; from *Zeit. Landw. Versuchs-Wesen Oesterr.*, 5, 1053—1062).—The method is based on the different solubilities of barium citrate and barium malate and admits of the detection of citric acid in the presence of malic acid. The wine is diluted with water or alcohol until it contains from 12 to 15 per cent. of alcohol, and then rendered feebly alkaline with ammonia; 50 c.c. are then

precipitated with barium chloride or barium acetate, and after keeping overnight the liquid is decanted on to a filter. The precipitate on the filter is washed back again with not more than 15 c.c. of water. After heating the moist precipitate to boiling, it is decomposed with sulphuric acid (1 : 10). From 1 to 2 c.c. of basic lead acetate and 1 to 2 c.c. of saturated lead acetate solution are added to the filtrate, which is then boiled and filtered. A milky turbidity of the filtrate on cooling indicates the presence of citric acid. Lead tartrate may separate later, but can be removed by subsequent heating and filtering.

W. P. S.

Methods of Determining Citric Acid in Commercial Citrates. VINCENZO OLIVERI (*Gazzetta*, 1902, 32, ii, 138—145).—It has been stated by Teschemacher and Ogston that in order to obtain concordant results for the amount of citric acid in calcium citrate by the two methods generally used, the alkalinity found by the older ignition method must be referred to the value 201 for the molecular weight of citric acid, whilst the acidity given by the new precipitation method must be calculated as citric acid by means of the molecular weight 210. The author has employed the two methods to analyse pure hydrated citric acid and six samples of commercial calcium citrate. The results, calculated on the molecular weight 210 for the acid, show that the old ignition method gives the more accurate numbers, those obtained by the precipitation method being from 1.5 to 3.5 per cent. lower than the others, according to the quantity of washing liquid employed and the duration of the operation. The errors produced by loss in the precipitation method hence lie between the limits of difference of the molecular weights 201 and 210. It is possible that the presence of oxalic, tartaric, malic, or other organic acid may have an influence on the results given by the ignition process, but such acids were not found in the six commercial citrates examined.

T. H. P.

Estimation of Tannic Acid. ED. CROUZEL (*Ann. Chim. anal.*, 1902, 7, 373—374).—The following process may be used for all the various tannins. The liquid, which should be freed, if necessary, from alcohol, is mixed with an excess of analgesin (phenyldimethylpyrazolone). To ensure the complete precipitation of the tannate, a quantity of sodium hydrogen carbonate amounting to double the weight of the analgesin is added. The precipitate is collected on a weighed filter, washed with water, dried at 100°, and weighed; half this weight represents tannic acid.

L. DE K.

Volumetric Estimation of Tannin and Analysis of Wood and Tannin Extracts. ALBERT THOMPSON (*Compt. rend.*, 1902, 135, 689—691).—The method of estimating tannin is based on the fact that it absorbs oxygen from hydrogen peroxide in the presence of alkali. The amount of oxygen present in the water, both before and after the oxidation of the tannin, can be estimated by adding pure lead dioxide; in the presence of alkali, the whole of the oxygen of the hydrogen peroxide is evolved when thus treated. One gram of the material in which the tannin is to be estimated is extracted with 50 c.c.

of 90 per cent. alcohol ; 25 c.c. are evaporated on the water-bath and the residue dissolved in 25 c.c. of water ; to 5 c.c. of this extract, 2 c.c. of hydrogen peroxide, in which the oxygen has been previously estimated, is added ; aqueous sodium hydroxide and lead dioxide are now introduced and the volume of oxygen evolved is measured. This method is perfectly trustworthy for estimating tannin which is capable of being absorbed by hide.

K. J. P. O.

New Process for Distinguishing between Raw and Boiled Milk. FRITZ URZ (*Chem. Zeit.*, 1902, 26, 1121—1122).—Two c.c. of milk are mixed with 0.5 c.c. of a mixture composed of 3 c.c. of 30 per cent. hydrogen peroxide and 97 c.c. of water, and a few drops of a *freshly prepared* alcoholic solution of Ursol O (0.1 gram in 30 c.c.) are added, and the whole well shaken. If the milk has been heated to 80° or above, the mixture remains white, but in the presence of even 5—10 per cent. of raw milk a blue colour is developed. Tabloids composed of lactose and a quantity of Ursol sufficient for one experiment will be found convenient in practice, as these keep for an indefinite time.

L. DE K.

Analysis of Butter Obtained from Separate Cows. J. KLEIN and A. KIRSTEN (*Milch Zeit.*, 1902, 31, 594—596 and 611—613).—The butters of 5 cows were examined, the samples being obtained at stated intervals during the lactation period. Full details of the feeding and condition of the cows are given, as are also the analytical results and curves showing the variations in the figures for each butter. The Reichert-Meissl values decreased as the lactation period progressed. One butter gave a value of 43.5—probably the highest known. The lowest figure obtained was 19.1 at the end of lactation. The insoluble fatty acids varied inversely with the Reichert-Meissl values. The highest iodine number (Hübl) obtained was 44.91, and the lowest 29.36 ; these numbers ran almost exactly parallel with the refractometer readings. The Köttstorfer values lay between 239.1 and 219.4. The feeding of the animals had some influence on the composition of the butters. In these experiments, the age of the cows did not appear to affect the results, but the authors believe that very old cows give butter of inferior quality.

W. P. S.

Colour Reaction of Oils. HANS KREIS (*Chem. Zeit.*, 1902, 26, 897, 1014).—Equal volumes of oil, nitric acid of sp. gr. 1.4, and an ethereal solution of phloroglucinol (1 : 1000) are in succession introduced into a test-tube and the whole well shaken. In the case of arachis oil, sesamé oil, cotton oil, nut oil, peach-kernel oil, or castor oil, the ethereal fatty layer shows an intense, raspberry-red colour. Olive oil, lard, or butter give no coloration, or at the most only a pale yellowish-red. The reaction may also be obtained by using solid phloroglucinol and nitric acid. Sesamé oil thus treated behaves in a peculiar manner. If 0.05 gram of phloroglucinol is placed in a test-tube and moistened with three or four drops of sesamé oil, and then with the same amount of nitric acid, the oil turns red and the acid intensely green. If the mass is now shaken with ether, this turns violet, and on

shaking with water this changes to a deep blue, whilst the ether becomes reddish-brown. The blue colouring matter, soluble in water, may also be obtained as follows: sesamé oil is diluted with 4 times its bulk of carbon tetrachloride, and to 2 c.c. of this mixture, 0.01 gram of phloroglucinol is added, then, carefully, 1 c.c. of nitric acid, and the whole is well shaken. The mixture assumes an intense greenish-blue colour, and on treatment with water yields an indigo-blue substance.

Oils which, on account of age or exposure, no longer give Bellier's resorcinol test also refuse to act with phloroglucinol. Such oils, however, when mixed with fresh sesamé oil, turn green when shaken with hydrochloric acid of sp. gr. 1.19; this coloration has been noticed by Bishop in the case of old samples of sesamé oil.

Sesamé oil, which does not give Bishop's reaction, at once shows it when mixed with other oils which have been bleached by exposure to light (Bishop-Kreis reaction).

When 2 c.c. of stale oil (olive, arachis, sesamé, cotton, poppy, or nut oil) are shaken in a test-tube with 2 c.c. of a cold saturated solution of resorcinol in benzene or an ethereal solution of phloroglucinol (1:1000), the acid acquires a permanent violet or red colour, which is not discharged by addition of water.

L. DE K.

Rapid Soap Analysis. FERNAND TELLE (*Ann. Chim. anal.*, 1902, 7, 367—370).—Two grams of the well-mixed sample are dissolved in 50 c.c. of hot water, to which, when cold, 10 c.c. of *N*-hydrochloric acid are added, the mixture being agitated in a separating funnel with 25 c.c. of ether. The aqueous layer having been removed, the ethereal layer is washed a few times with a little water, and finally evaporated in a weighed dish; the residual fatty acids are dried at 95° and weighed. The aqueous liquid is then titrated with *N*-sodium hydroxide, using phenolphthalein as indicator; the number of c.c. used for neutralisation deducted from 10 gives the amount of alkali present in the soap. The amount of free alkali (which also includes alkali carbonate) is estimated by boiling 2 grams of the sample for half-an-hour in a reflux apparatus with 20 c.c. of *N*/10 alcoholic oleic acid diluted with 50 c.c. of alcohol; in another apparatus, 20 c.c. of oleic acid solution and 50 c.c. of alcohol are boiled for the same length of time, and both liquids are then titrated with *N*/10 aqueous sodium hydroxide. The difference between the two titrations represents the free alkali.

L. DE K.

A New Reaction of Formaldehyde. MANGET and MARION (*Compt. rend.*, 1902, 135, 584).—The presence of formaldehyde in milk can be detected by adding a small quantity of amidol (1:2:4-diaminophenol) or aminophenol, when a yellowish colour is produced; with normal milk, the colour is salmon.

By adding a crystal of amidol to a beef jelly containing formaldehyde, a yellowish colour is produced which becomes deeper on the addition of ammonia; if no formaldehyde is present, a rose colour is formed, which becomes blue on the addition of ammonia.

J. McC.

Amine-ammonia Water obtained by the Distillation of the Concentrated Waste-liquors from the Desaccharification of Molasses. KARL ANDRLÍK (*Zeit. Zuckerind. Böhm.*, 1902, 27, 1—15).—The so-called ammonia-water obtained by the Fischer-Štěrba process of distillation of the residual liquors from the desaccharification of molasses should really be called amine-ammonia water, one-quarter to one-third of the total nitrogen present being in the form of ammonia, and the rest as mono-, di-, and tri-methylamines, other amines and pyrrole, pyridine, &c.; methyl alcohol also occurs in the liquid. Separation of the ammonia and the various amines cannot be effected by fractional distillation with lime. By the method proposed by Bresler (*Zeit. Ver. deut. Zuckerind.*, 1900, 25, 1627) for the separation of these nitrogen compounds, the ammonia can be determined exactly and the methylamine approximately. The di- and tri-methylamines cannot be separated by treating the mixed platinichlorides either with 80 per cent. or absolute alcohol, the former dissolving some of the dimethylamine salt and the latter leaving undissolved a portion of the trimethylamine compound. T. H. P.

Occurrence and Properties of Choline. HEINRICH STRUVE (*Zeit. anal. Chem.*, 1902, 41, 544—550).—When the development of the buds of the vine commences in the spring, colourless exudations, about the size of a small pin's head, appear on the young leaf-stalks. If these are crushed and treated with Florence's iodine reagent, they exhibit a copious formation of iodocholine crystals. Choline can also be detected in all samples of commercial cream of tartar. The filtered aqueous solution of the substance is made alkaline with lime and evaporated to dryness. The residue is extracted with strong alcohol, and, after evaporating the alcohol, the iodine test is applied. The author has failed to find a method of estimating choline quantitatively. Whilst confirming Gulewitsche's statement that it can be detected by phosphomolybdic acid, phosphotungstic acid, or iodine at a dilution of 1:400, he finds that the presence of other substances may hinder its precipitation altogether. The sugar and glycerol in an alcoholic extract of a wine residue completely prevent the precipitation of choline by platinic chloride. M. J. S.

Estimation of Urea in Urine. OTTO FOLIN (*Zeit. physiol. Chem.*, 1902, 36, 333—342).—To insure complete decomposition of the urea in the process previously described by the author (*Abstr.*, 1901, ii, 630), the boiling with magnesium chloride should be continued for 45 minutes. A bent safety tube at the top of the reflux-condenser is also advisable. The distillation of the ammonia formed takes at least an hour, as some of the nitrogen is converted into cyanogen compounds, which are only slowly decomposed by boiling alkali solution.

Referring to the low results obtained with this method by Arnold and Mentzel (this vol., ii, 48), the author states that their inaccurate figures were due to not having followed the method as originally described, and, further, that pure uric acid and hippuric acid do not yield any ammonia when treated according to this method.

W. P. S.

Evaluation of Opium. C. REICHARD (*Chem. Zeit.*, 1902, 26, 1095—1099).—A criticism of an article on opium assay in "E. Merck's Bericht," 1901, unsuitable for useful abstraction. The author thinks there may be a future for his silver process (*Abstr.*, 1901, ii, 707).
L. DE K.

Analysis of Preparations containing Opium. ALFRED H. ALLEN and GEORGE E. SCOTT-SMITH (*Analyst*, 1902, 27, 350—355).—Methods are given for the estimation of camphor, alcohol, and benzoic acid in paregoric and cough mixtures of various kinds. The quantity of opium in paregoric is generally too small to allow it to be estimated, but meconic acid, proving the presence of opium, may be detected by applying the ferric chloride test to the ethereal solution obtained on extracting the neutralised benzoic acid with ether. Particular attention is drawn to the fact that cough mixtures almost always contain ipecacuanha and that the alkaloids of the latter may be, and have been, mistaken for those of opium. Both groups of alkaloids give somewhat similar colour reactions with Fröhde's reagent (sulphomolybdic acid), reduce iodic acid, and yield a blue colour with a mixture of ferric chloride and potassium ferricyanide. The microscopic crystals of the ipecacuanha alkaloids, however, in no way resemble the characteristic crystals of morphine.
W. P. S.

Certain Reactions of the Alkaloids of Ipecacuanha. ALFRED H. ALLEN and GEORGE E. SCOTT-SMITH (*Analyst*, 1902, 27, 345—349).—The reactions refer to the three alkaloids, emetine, cephaeline and psychotrine. The mixed alkaloids give, with ferric chloride, a blue coloration changing to green. With Fröhde's reagent, the colours vary from bluish-purple to violet, resembling those given by mixed opium alkaloids. Some extracts of ipecacuanha give an immediate blue coloration with starch and iodic acid. Psychotrine appears to be the alkaloid which yields the colour reactions with ferric chloride and iodic acid, but the authors believe that another substance is present which partly accounts for the colorations. The following table shows the reactions of the separate alkaloids:

Reagent.	Emetine.	Cephaeline.	Psychotrine.
Ferric chloride	Indefinite	{ Bluish-green (B) Indefinite (C)	{ Pale cherry-red (B) Indefinite (C)
Fröhde's reagent	{ Dirty green (B) Bluish (C)	{ Pink, changing to green (B) Reddish-purple (C)	{ Pale pink (B) Dull purple (C)
Fröhde's reagent and hydrochloric acid..	Grass-green	Prussian blue	{ Pale pink, changing to pale green Blue
Starch and iodic acid...	Negative	Negative	Blue
Ferric chloride and potassium ferri- cyanide	Gradual blue coloration	{ Almost immediate blue (C) Immediate blue (B)	{ Immediate blue

B denotes Brazilian, and C Columbian (Cartagena) ipecacuanha. Microscopic crystals of psychotrine resemble crystals of arsenic trioxide or, sometimes, rice granules.
W. P. S.

Detection of Pilocarpine and Reactions for Apomorphine. A. WANGERIN (*Chem. Centr.*, 1902, ii, 1009—1010 ; from *Pharm. Zeit.*, 47, 739—740).—When 1 c.c. of a freshly prepared 1 per cent. solution of apomorphine hydrochloride is shaken with 4 drops of 0.3 per cent. potassium dichromate solution, the yellowish-green coloration changes to dark green. On shaking the solution with 10 c.c. of ethyl acetate, the latter becomes violet. By adding 5 drops of stannous chloride solution and shaking, the violet coloration is changed to green, but is restored by the addition of a few drops of potassium dichromate. Using ether instead of ethyl acetate, the reaction is not so sharp, whilst benzene, toluene, xylene, carbon disulphide, and carbon tetrachloride are unsuitable. Chloroform may be used, in which case the addition of stannous chloride gives an indigo-blue coloration not altered by potassium dichromate. With amyl alcohol, a blue coloration is obtained, turning green on addition of stannous chloride, and yellow when a further quantity of potassium dichromate is added. Pilocarpine, when oxidised with potassium dichromate and hydrogen peroxide, gives blue or violet coloured solutions on the addition of ether, ethyl acetate, and amyl alcohol. Very little of the colour dissolves in light petroleum, carbon disulphide, or carbon tetrachloride. An excess of stannous chloride destroys the coloration.

W. P. S.

Evaluation of Digitalis Leaves. HANS ZIEGENBEIN (*Arch. Pharm.*, 1902, 240, 454—470).—An alcoholic extract of the leaves was prepared, and the residue left after this had been concentrated was diluted with water ; increasing quantities of this solution were injected into the lymph sac of a frog, and the minimum dose was thus found which produced paralysis of the heart's action. This varied between limits corresponding with 0.03 to 0.06 gram of the dried leaves per 100 grams of the body weight of the frog, according to the locality from which the leaves came and the commercial fineness of the sample ; it was as high as 0.1 gram in the case of leaves which had been coarsely powdered and kept for a couple of years, and was also high in the case of a comparatively recent sample which had been powdered finely. There is no relation between the percentage of digitoxin and the toxicological action, and therefore the percentage of digitoxin in the drug does not indicate its therapeutic value. The digitoxin was estimated by Keller's method as improved by Fromme ; it was dissolved in dilute alcohol, and the toxicological action of this solution was also determined. This was always less than that of an extract of the leaves, corresponding with the same weight of dried leaves for the same volume of solution but containing the other glucosides in addition ; it stood in no constant relation to the latter, but varied between 3 and 7 times less from case to case.

C. F. B.

Detection of Chestnut Tree Extract in Oak Extract. FERDINAND JEAN (*Compt. rend.*, 1902, 135, 536—537).—Chestnut tree extract liberates iodine from a solution of iodic acid, but oak extract and the other ordinary wood extracts do not give this reaction, with the exception of campeachy wood extract, which liberates a small quantity of iodine. The oak extract is repeatedly agitated with an

aqueous solution of iodic acid and carbon disulphide, chloroform, benzene, or carbon tetrachloride, the latter being afterwards separated in the usual way. The liberation of iodine shows the presence of chestnut wood extract, and the quantity of iodine can be estimated by titration; 1 part of iodine corresponds with 6.25 parts of dry chestnut tree extract, 19 parts of extract of 20° B, or 16 parts of extract of 25° B.

C. H. B.

Detection of Proteids, &c., in Urine. MAURICE BERNARD (*Chem. Centr.*, 1902, ii, 828; from *Pharm. Zeit.*, 47, 657).—A turbidity or precipitate on adding a little acetic acid in the cold points to pyin or mucin. The liquid is decanted and the deposit treated with ammonia, which, in the presence of pyin, forms a slimy solution; mucin may be suspected when the urine sediment contains but few leucocytes but many epithelial cells. The filtrate from the pyin and mucin is mixed with a few drops of Tanret's reagent (3.32 parts of potassium iodide, 1.35 of mercuric chloride, 20 of acetic acid, and 10 of water). A precipitate or turbidity shows globulin or serum-albumin; globulin may be detected by adding to the carefully neutralised original sample a saturated solution of magnesium sulphate, and the serum-albumin may be precipitated in the filtrate by warming and adding a little trichloroacetic acid. To the filtrate from the serum-albumin is added a solution of potassium ferrocyanide in acetic acid: a precipitate, disappearing on warming but reappearing on cooling and soluble in sodium hydrogen carbonate, is due to the presence of albumoses. A precipitate obtained in the cold with ferrocyanide after removing proteids in the original urine with Tanret's reagent, which disappears on warming but reappears on cooling, is due to peptones. The estimation of serum-albumin is effected as follows: 100 c.c. of the filtered urine are freed from nucleoalbumins and globulin and if the sp. gr. should be below 1.015, 2 to 5 grams of sodium sulphate are also added. After adding a few drops of trichloroacetic acid, the liquid is heated to boiling, a few drops more of the acid are added, and the boiling is continued for half a minute longer. The coagulated albumin is collected on a weighed filter, washed with water acidified with acetic acid, then with alcohol and ether, and finally dried at 105° and weighed.

L. DE K.

Estimation of Moist Gluten in Flour. MARCEL ARPIN (*Ann. Chim. anal.*, 1902, 7, 325–331, 376–381, 416–420).—A criticism of the method of judging the quality of flour by the amount of moist gluten obtained therefrom. Tables are given showing the effect of the temperature, the time the dough is kept before washing out the starch, the time of washing, and the nature of the water. Gluten is perceptibly soluble in pure water, but a moderate amount of temporary hardness diminishes the solubility. The results are more concordant and nearer the truth when the gluten is dried at 105° before being weighed, but even then the process is only an approximate one. It is therefore proposed to estimate the gluten (which practically means the whole of the albuminous matters) by Kjeldahl's nitrogen process.

L. DE K.

Modification of Huppert's Test for Bile Pigment. M. NAKAYAMA (*Zeit. physiol. Chem.*, 1902, 36, 398—400).—The following is the new method of performing the test, which is more delicate than Huppert's. Five c.c. of icteric urine, mixed with an equal volume of a 10 per cent. solution of barium chloride, are centrifugalised. The clear fluid is decanted and the precipitate treated with 2 c.c. of a reagent consisting of 99 parts of 95 per cent. alcohol and 1 part of fuming nitric acid which contains 4 grams of ferric chloride per litre, the mixture being stirred and heated to boiling. The supernatant liquid assumes a green or blue-green colour, which, on the addition of fuming nitric acid, changes to violet and red.

W. D. H.

Action of Hydrogen Peroxide on Blood. JULES VILLE and JOSEPH MOITESSIER (*Bull. Soc. chim.*, 1902, 27, [iii], 1003—1008. Compare Cotton, *Abstr.*, 1901, ii, 295).—When a solution of hydrogen peroxide is mixed with defibrinated blood, the amount of oxygen disengaged is dependent on the masses of the reacting ingredients. It increases with the proportion of peroxide to a maximum and then diminishes, the maxima varying with each kind of blood (compare Cotton, *loc. cit.*); it is increased by previous dilution of the blood with water; it is diminished to a minimum and then increased by previous dilution of the hydrogen peroxide solution. The activity of the latter is also greatly diminished by the presence of sulphuric acid. These observations are explained by assuming that blood contains substances other than hæmoglobin and fibrinogen which react with hydrogen peroxide.

T. A. H.

Estimation of the Ferment-secretions in the Stomach, Based on the Action of the Fat-destroying Enzymes. FRANZ VOLHARD [and, in part, STADE] (*Chem. Centr.*, 1902, ii, 947—948; from *Verh. Deut. Naturf. u. Aerzte.*, 1902, 2, 43—47. Compare *Abstr.*, 1901, ii, 518).—Instead of proceeding as in the method originally given for the extraction of the powder containing the fat, it is better to shake the digested mass with a mixture of 75 c.c. of ether and 2 c.c. of alcohol. To 50 c.c. of the ethereal layer, 75 c.c. of alcohol are added, the solution is titrated and boiled for 6 hours on a water-bath with 10 c.c. *N*-potassium hydroxide, 10 c.c. of *N*-hydrochloric acid are then added, and the solution titrated back with *N*/10 alkali. The ratio between the decomposed and undecomposed fat is thus obtained. In this way, further action of the enzyme during the drying of the kaolin mixture is avoided.

As the result of further experiments on these lines, the authors state (contrary to their former conclusion) that the action regularly increases in proportion to the time, so far confirming Schütz-Borissow's statement that the amount of enzyme may be calculated from the digestive products formed.

W. P. S.

General and Physical Chemistry.

Refractive Powers of Hydrocarbons with Heterocyclic Chains. GIOVANNI PELLINI and DOMENICO LOI (*Gazzetta*, 1902, 32, ii, 197—208. Compare Chilesotti, *Abstr.*, 1900, i, 339, and Pellini, *Abstr.*, 1901, ii, 365.)—Measurements have been made of the refractive indices for the H_α , H_β , H_γ , and sodium lines of the spectrum, of acridine, dihydroacridine, α -naphthaquinoline, tetrahydro- α -naphthaquinoline, β -naphthaquinoline, and tetrahydro- β -naphthaquinoline in benzene solutions. The following table contains the experimental numbers for the molecular refractions for the H_α line together with the corresponding calculated values :

	Per cent. in solution.	$M \cdot \frac{\mu_{H_\alpha} - 1}{d}$			$M \cdot \frac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}$		
		Found.	Calc.	Diff.	Found.	Calc.	Diff.
Acridine	8.6930	111.66	96.26	+15.61	62.61	54.99	+7.49
"	15.6954	112.09	—		62.36	—	
Dihydroacridine	3.2151	99.86	98.86	+0.81	56.90	57.07	+0.14
"	2.5991	99.49	—		57.56	—	
α -Naphthaquinoline ...	7.36325	106.46	96.26	+10.91	60.53	54.99	+5.35
"	7.84836	107.89	—		60.16	—	
Tetrahydro- α -naphthaquinoline	10.6363	109.42	99.06	+10.71	61.12	57.37	+3.99
Tetrahydro- α -naphthaquinoline	4.7774	110.12	—		61.61	—	
β -Naphthaquinoline ...	15.5370	105.92	99.26	+9.58	60.05	54.99	+4.87
"	15.7392	105.77	—		59.67	—	
Tetrahydro- β -naphthaquinoline	8.54624	107.71	99.06	+7.85	61.06	57.37	+3.66
Tetrahydro- β -naphthaquinoline	7.4685	106.12	—		61.01	—	

It will be seen from these figures that the molecular refraction of acridine exhibits a large increase on the calculated value. Whilst, however, the excess in the value for quinoline is equal to that observed in the corresponding naphthalene group, in the case of acridine the molecular refraction is much greater than that of anthracene; the latter compound shows excesses over the calculated number of 11.94 and 5.35 for the Gladstone and Lorenz and Lorentz formulæ respectively. When, however, acridine is hydrogenised, the experimental and calculated numbers agree, as they do also for dihydroanthracene. In the formation of the last-named compound, the so-called Gladstone

carbon atoms of the anthracene (namely, those which are united by all their bonds to other doubly-linked carbon atoms) are destroyed.

It would therefore appear as if the carbon atoms connecting two nuclei may be combined with other carbon atoms united in their turn with atoms of varying nature and yet have an influence on the refractive power analogous to that of true Gladstone atoms.

As regards the hypothesis of centric valencies, it would seem that this cannot be applied to the case of heterocyclic molecules, the influence of a centric linking varying widely for the different compounds, as is seen from the following table, the numbers in which are calculated for the Gladstone formula :

	Number of centric bonds.	Mol. refraction.			Value of the centric bond.
		Found.	Calc.	Diff.	
Quinoline	12	73.03	59.26	13.77	1.14
Acridine	18	111.87	81.86	30.01	1.66
α -Naphthaquinoline	18	107.17	81.86	25.31	1.40
β -Naphthaquinoline.....	18	105.84	81.86	23.98	1.33

For the Lorenz and Lorentz formula, the respective values for the centric bond are 0.75, 0.95, 0.83, and 0.80. For homocyclic nuclei, on the other hand, the increase of the molecular refraction due to the centric bond is constant, and has the value 1.46 for the μ formula and 0.89 for the μ^2 formula.

T. H. P.

Spectroscopic Methods. HEINRICH KONEN (*Ann. Physik*, 1902, [iv], 9, 742—780).—The author has made an exhaustive study of the spectra obtained when an electric discharge passes in various liquids between poles of metal or carbon. The arc spectrum, apparently, is dependent only on the nature of the metallic poles and not on the character of the surrounding liquid; when the poles are of carbon, there is sometimes a slight indication in the spectrum of the nature of the surrounding liquid. The question of the origin of the Swan spectrum (compare Smithells, *Abstr.*, 1901, ii, 366; Baly and Syers, *Abstr.*, 1901, ii, 633) is discussed at length, but no decisive experimental evidence is brought forward.

J. C. P.

Spectrum of Lithium. AUGUST HAGENBACH (*Ann. Physik*, 1902, [iv], 9, 729—741).—As is well known, the line spectra of the alkali metals, with the exception of lithium, have been analysed into primary and secondary series consisting of pairs of lines, and the differences between the reciprocal wave-lengths for such pairs have been found to be nearly proportional to the square root of the atomic weight of the metal. The author now shows that in the case also of lithium, such a pair exists at 4603. The difference of the reciprocal wave-lengths of the two lines is only very approximately proportional to the square root of the atomic weight.

J. C. P.

Fluorescence and Phosphorescence of Diamonds and Their Influence on the Photographic Plate. OTTO ROSENHEIM (*Chem. News*, 1902, 86, 247).—Every diamond, but not carbonados, examined by the author, fluoresced under the influence of polonium, and the rays emitted were photographically active, but differed from those from the polonium by their power of penetrating various media, glass, paper, celluloid, &c. On the other hand, only a few diamonds phosphoresced after exposure to magnesium light, and the phosphorescent rays did not affect the photographic plate. D. A. L.

Measurements on the Magnetic Rotation of the Plane of Polarisation in Liquefied Gases under Atmospheric Pressure. II. Measurements with Methyl Chloride. L. H. SIERTSEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 243—247).—Defects in the apparatus previously employed are pointed out and an improved form is described, diagrams being added. Determinations of the magnetic rotation of liquid methyl chloride at atmospheric pressure were again made; the rotation constant was found to be 0.01372 for sodium light, and the rotation dispersion normal, differing little from that of gases or water. The values of the ratio ρ/ρ_D obtained for different wave-lengths included:

λ .	ρ/ρ_D .	λ .	ρ/ρ_D .
420	2.003	(589)	1.000
512	1.351	604	0.947
555	1.145	659	0.794

(compare Abstr., 1901, ii, 5).

L. M. J.

Photoelectric Action. THEODOR WULF (*Ann. Physik*, 1902, [iv], 9, 946—963).—Under the action of ultra-violet rays, the dissipation of a negative charge from a platinum electrode polarised with hydrogen is much more rapid than from one polarised with oxygen, chlorine, or ozone, and the order of photoelectric efficiency is also the order of electrolytic potential. The nature of the medium surrounding the electrode is of importance, and it seems probable that the greater the chemical potential difference between the electrode and the surrounding atmosphere, the greater is the photoelectric action; it is further probable that the dissipation of electricity by light is associated with some chemical process.

In the course of the investigation, a lamp has been devised for the combustion of carbon bisulphide in oxygen; the light so obtained was very steady and effective. J. C. P.

Excited Radioactivity and Ionisation of the Atmosphere. E. RUTHERFORD and S. J. ALLEN (*Phil. Mag.*, 1902, [vi], 4, 704—723).—Elster and Geitel have shown that a negatively charged conductor placed in the open air becomes temporarily radioactive. With the help of a sensitive quadrant electrometer, the authors have studied this excited radioactivity and the ionisation of air. A long wire was negatively charged and hung for several hours in the open air; it was

then wound on a frame and suspended in a metal cylinder kept at a fixed potential, the wire itself being connected with the electrometer. The radiation from the wire ionised the air inside the cylinder, and there was, therefore, a gradual decay of the excited radioactivity. The rate of decay is regular, independent of the nature and diameter of the wire and of the negative potential during exposure. This is analogous to what is known of the excited radiations produced by thorium and radium (compare Rutherford and Brooks, *Abstr.*, 1902, ii, 590). The amount of excited radioactivity, on the other hand, varies greatly with the weather and the wind, and increases with the voltage of the exposed wire. The excited radiation produced in air, as described above, has a penetrating power greater than the radiations, not deviated by a magnetic field; from uranium, thorium, and radium, and greater than the excited radioactivity due to radium and thorium (compare Rutherford and Brooks, *loc. cit.*). There seems to be little doubt that the excited activity is due to a deposit of a minute quantity of intensely active radioactive matter.

An apparatus is described for determining the number of ions produced per c.c. per second in air and for tracing the variation of the ionisation current with the strength of the electric field. The number of ions produced per c.c. per second was thus found to be 15, a number not very different from that found by Wilson by another method (*Abstr.*, 1901, ii, 435).

J. C. P.

Heat and Light Radiations of Certain Oxides. CH. FÉRY (*Ann. Chim. Phys.*, 1902, [vii], 27, 433—548).—The total radiations, both luminous and non-luminous at 500—1700°, were investigated in the case of retort carbon, chromium sesquioxide, platinum, the oxides of calcium, magnesium, zirconium, lanthanum, thorium, cerium, and the mixture used in the Auer lamp (thorium 98.7 and cerium 1.3 per cent.). For the source of heat, a modified Bunsen burner was used; the temperature was measured by means of a thermoelectric pile, one junction of which, carrying a small quantity of the substance under investigation, was kept in rapid rotation in the flame. The total radiation was measured by a thermoelectric pile, and the luminous radiation by comparing a given wave-length in the green ($0.562 \mu\mu$) with a similar wave-length of known luminosity, the assumption being made that the total luminous radiation was proportional to the monochromatic radiation in the green. The oxides of calcium, thorium, and lanthanum and the Auer lamp mixture show, at a given temperature, a higher total radiation in the oxidising than in the reducing flame; cerium, on the other hand, a lower radiation; a similar relation holds for the luminous radiations, except that the Auer lamp mixture gives a higher value in the reducing flame. The colour of the light emitted by the various oxides in the oxidising and reducing flame is different.

The major portion of the paper deals with matter mainly of physical interest. The conclusion is drawn from the observations that at high temperatures the oxides suffer both chemical and physical changes.

As regards the part played by the constituents of the Auer lamp mixture, the opinion is expressed that the cerium intensifies locally

the chemical action owing to its power of condensing gases on its surface, and thus brings about a raising of the temperature; the thorium merely acts as a medium for diffusing the cerium, and at the same time has the advantage of being transparent to radiations.

K. J. P. O.

Researches on Voltaic Elements founded on the Reciprocal Action of Two Saline Liquids. MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], 27, 289—328, 328—348. Compare this vol., ii, 51).—A continuation of a more detailed account of work which has previously been published (Abstr., 1902, ii, 375, 376, 439, 440, 546, 547, 591, and this vol., ii, 3).

K. J. P. O.

Ionisation of a Flame containing Salt. GEORGES MOREAU (*Compt. rend.*, 1902, 135, 898—900).—The conductivity of a flame containing salt at a constant temperature depends on the *E.M.F.*, the distance between the electrodes, which consist of small, flat, platinum condensers plunged in the flame, and the concentration of the salt solution, the evaporation of which gives the salt to the flame. The results show that there is no dissociation in the vapour of the salt before the introduction of the electrodes; the conductivity of the flame is unipolar, ionisation occurring mainly at the negative electrode, and is thus analogous to the conductivity of gases in the neighbourhood of a metal illuminated with ultra-violet light. The current is given by the equation $I = I_0(1 - e^{-kx})$, where e is the base of the Napierian logarithms, x the distance between the electrodes, and I_0 a function varying with the electric field, the temperature, and the nature of the metal in the salt; k is independent of the salt and of the field, but varies slowly with temperature. It is supposed that on the negative electrode, electrons are formed which ionise the salt vapour in much the same way as do the emanations from uranium.

K. J. P. O.

Behaviour of Water relatively to Air. FRIEDRICH KOHL-RAUSCH (*Zeit. physikal. Chem.*, 1902, 42, 193—201).—The author has studied the influence of the atmosphere on the conductivity of water, and describes methods of obtaining pure water which will not deteriorate on contact with air if ordinary precautions are taken. One simple method of freeing the water in a flask from carbon dioxide is to place a collar of slaked lime on the outside of the neck, and to protect the lime from contact with the atmosphere by means of an inverted beaker; this effects a reduction in the conductivity of a large quantity of water from 0.9×10^{-6} to 0.5×10^{-6} in the course of a few days. The conductivity can be reduced to 0.3×10^{-6} either by simple contact with platinum electrodes or by the passage of a current of air freed from carbon dioxide through the cell containing the electrodes (not platinised).

The author indicates the precautions that are necessary in handling such pure water if its conductivity is to remain constant. The water should not be stored in the laboratory, and the stopper of the containing vessel should be protected against dust. The breath is a very common source of contamination, and transference of the water from one vessel to another should take place at an open window; on no account

must the water be blown from a wash-bottle. Water of conductivity 1.0×10^{-6} improves by prolonged passage of air from the open, but deteriorates at once if shaken in a room in which there is a person or a flame.

J. C. P.

Equivalent Conductivity of the Hydrogen Ion derived from Transference Experiments with Hydrochloric Acid. ARTHUR A. NOYES and G. V. SAMMET (*J. Amer. Chem. Soc.*, 1902, 24, 944—968).—The apparatus previously described (Abstr., 1901, ii, 143) was used in the determination. In order to prevent the introduction of any foreign salts, a silver anode was used, and precautions were taken, by using a low current-density, against evolution of chlorine. *N*/20 and *N*/60 hydrochloric acid solutions were used. The current was passed through for three hours at constant temperature and the quantity of electricity was measured by a silver voltameter. The liquid was divided into five portions, one at the anode, one at the cathode, and three in the middle, and each was titrated with standard barium hydroxide solution and also analysed by precipitation with silver nitrate. For the transference number at 20°, the *N*/20 solution gave 165.69 (the values given have been multiplied by 10^{-3}) with an average deviation of 0.12; the *N*/60 solution gave 167.43 with an average deviation of 0.25; at 10°, the *N*/20 solution gave 158.62 with an average deviation of 0.15, and the *N*/60 solution 177.34 with an average deviation of 0.16. It is shown that the error does not, in all probability, exceed 0.45 per cent. It is not known to what extent the difference in the results of the two solutions is due to change of concentration, as it may partially be accounted for by experimental error, and it must be admitted that an error of 1 to 2 per cent. might be made by assuming no further change in the transference number after *N*/60 is reached, although this is not probable.

The conductivity of *N*/58 and *N*/252 hydrochloric acid was determined at 10°, 20°, and 30°; the results agree to within 1 per cent. with those of Kohlrausch and Déguisne, and the temperature coefficient (1.606) agrees even more closely.

From previous determinations of the conductivity of potassium chloride, the authors calculate the mobilities of the chlorine ion to be 54.5 at 10°, 68.5 at 20°, and 83.3 at 30°, and, further, the following values for the equivalent conductivity of completely dissociated hydrochloric acid and the mobility of the hydrogen ion:

	10°	18°	20°	25°	30°
H' + Cl'	343.2	395.5	408.5	440.7	472.4
H'	288.7	329.8	340.0	364.9	389.1

The error in this final result cannot exceed at the outside 0.8 per cent. The value at 25° is greater by 5.8 per cent. than that calculated by Ostwald, and 3.8 per cent. greater than that calculated by Kohlrausch for 18°.

J. McC.

Electrical Conductivity of Potassium Chloride in Mixtures of Water and Ethyl Alcohol. W. A. ROTH (*Zeit. physikal. Chem.*, 1902, 42, 209—224).—Careful determinations (accurate to 0.1 per

cent.) of the conductivity of potassium chloride in 8 and 20.3 per cent. alcohol at 18° have been made, the range of concentration being from $V=30$ to $V=600$. It is found that the molecular conductivity Λ decreases as the percentage of alcohol increases, but the percentage decrease becomes less as the quantity of alcohol increases. The variation of the conductivity with the dilution is represented for a given alcohol concentration by the formula $(\Lambda_{\infty} - \Lambda)/\Lambda^p = c \cdot \eta^{\frac{1}{2}}$ (compare Kohlrausch, Abstr., 1901, ii, 221); the older formula, $\Lambda_{\infty} - \Lambda = c \cdot \eta^{\frac{1}{2}}$ (Kohlrausch, Abstr., 1894, ii, 79), is inadequate.

The ratio $\Lambda_{H_2O}/\Lambda_{Alc}$ decreases as V increases, and it must therefore be supposed that both the mobility of the ions and the degree of dissociation are diminished by the addition of alcohol. The formula given by Arrhenius (Abstr., 1892, 1038), $\Lambda_{Alc} = \Lambda_{H_2O}(1 + ap/2)^2$, where p is the percentage of alcohol by volume, is found to hold up to $p=10$.

The temperature coefficient of conductivity rises rapidly as the percentage of alcohol increases, slowly as V increases, so that the ratio $\Lambda_{H_2O}/\Lambda_{Alc}$ decreases as the temperature rises.

The formula $\Delta/p(100 - p) = \text{const.}$ (Wakeman, Abstr., 1893, ii, 257), in which Δ is the fall in value of the ionic mobility corresponding with the addition of p per cent. by volume of alcohol, holds fairly accurately for both the alcohol concentrations used in this investigation.

When Λ/Λ_{∞} is taken as the degree of dissociation, it is found that of the formulæ for a dissociation constant given by Ostwald, Rudolphi, and van't Hoff, none leads to satisfactory results. J. C. P.

Electrical Conductivity of Compressed Powders. FRANZ STREINTZ (*Ann. Physik*, 1902, [iv], 9, 854—885).—In continuation of a previous investigation (Abstr., 1900, ii, 641), a number of metallic oxides and sulphides have been examined. All white, yellow, red, and grey compounds are non-conductors, and at the ordinary temperature only those dark coloured compounds are conductors which can be compressed into compact masses exhibiting metallic lustre and hardness; in no case was evidence obtained of electrolytic conduction.

The compounds that conduct fairly well at the ordinary temperature (such as lead dioxide, cuprous and cupric sulphides) have a positive resistance-temperature coefficient, much smaller, however, than that of metals. On the other hand, the electrical behaviour of compounds which exhibit only a small conductivity at the ordinary temperature (such as manganese dioxide, lead, mercuric and silver sulphides) is very much affected by change of temperature. In certain cases (such as cadmium oxide), the conductivity and its temperature coefficient exhibit rather marked differences for different temperature ranges—an observation which leads the author to suggest the existence of more than one form of the substance. If this view is accepted, cadmium oxide would have a transition point about 200°. J. C. P.

Diminution of Cathodic Depolarisation by Potassium Chromate. ERICH MÜLLER (*Zeit. Elektrochem.*, 1902, 8, 909—914. Compare Abstr., 1901, ii, 218).—Potassium iodate is reduced, in alkaline

solution, at a lower potential than potassium chromate. For this reason, no hydrogen is evolved when an alkaline solution of potassium iodate and chromate is electrolysed with a small cathodic current density, the iodate being reduced; when the current density is increased, the *P.D.* at the cathode soon reaches the value at which chromate is reduced, a film of an oxide of chromium is formed on the cathode and hydrogen is evolved, no further reduction of iodate taking place. The film once formed is fairly stable; it survives an interruption of the current for 15 minutes, but not for 30 minutes. At 75°, periodate is formed, and the chromium oxide film breaks down when its concentration reaches a certain limit. It is found that periodate oxidises chromic oxide to chromium trioxide, whilst iodate does not. Solutions of chromates cannot be reduced to chromic oxide owing to the formation of the film on the cathode, but if a mercury cathode is used, on which a coherent film cannot form, the reduction becomes possible.

T. E.

Dissociation of Electrolytes. C. LIEBENOW (*Zeit. Elektrochem.*, 1902, 8, 933).—Equilibrium between the ions and the molecules of an electrolyte exists when equal numbers of molecules are split up into, and formed from, ions in unit time. Assuming the molecules to consist of oppositely charged portions held together by the attractions of the charges, then this attraction will be diminished in proportion to the dielectric constant of the solvent. The attraction of the free ionic charges for the one half of the electron molecule attached to the undissociated molecule and their repulsion of the other half will produce another force tending to split up the molecule. This force is proportional to the square of the distance between the ions and the undissociated molecules or to the $2/3$ power of the concentration of the ions. It is also proportional to the number of charges carried by an ion. Setting out from these considerations, the author arrives at the following formula for the relation between the concentrations of the ions and the undissociated molecules in a solution of a binary electrolyte, $x^2(x-y) = A + Bx^{2/3}$, where x is the concentration of an ion, y the total concentration of the electrolyte, A a constant which is proportional to the number of molecules which dissociate into ions in unit time independently of the ionic attractions, and B a similar constant for the dissociation under the influence of the ionic attractions. Using the values $A = 0.027$, $B = 2.75$, and $\lambda\infty = 130.1$ (λ = molecular conductivity at 18°), the author shows that his formula permits the conductivities of solutions of potassium chloride to be calculated with an error not exceeding 1 per cent.

T. E.

The Passage of a Direct Current through an Electrolytic Cell. SAMUEL L. BIGELOW (*J. Physical Chem.*, 1902, 6, 603—628).—Various explanations have been offered for the cause of the current through an electrolyte produced by an *E.M.F.* less than the decomposition *E.M.F.*, but none, in the author's opinion, is completely satisfactory. His own experiments show that with an *E.M.F.* of 1 volt, a current is produced in an aqueous solution of sulphuric acid which decreases with time to a minimum value of about 0.2 microamperes.

Shaking or wiping the electrodes caused a considerable increase, which, however, passes off in a few minutes, the original minimum being again attained. The minimum current obtained with a $N/2$ solution of sulphuric acid was practically identical with that obtained in a $N/200$ solution, and from this fact the author considers that the current is not carried by the ions resulting from the dissociation of the electrolyte. The temperature coefficient of the current was found to be greatly in excess of the average rate of increase of conductivity of an electrolyte. Temporary small variations of the *E.M.F.* do not produce any permanent effect on the residual current. The author considers that such conductivity can be explained best on the assumption that the molecules themselves are also able to carry electrical charges, just as the molecules of a rarefied gas do, and this would further explain the behaviour of solutions which conduct electricity, although cryoscopic methods indicate no dissociation.

L. M. J.

Principle of Electrolytic Dissociation and Conductivity in Gases, Electrolytes, and Metals. J. STARK (*Chem. Centr.*, 1902, ii, 1171—1172. From *Naturw. Rundsch.*, 1902, 17, 533—536).—When the elements are arranged in the order of their ionic energies, a series is obtained beginning with the electronegative elements and ending with the electropositive elements. By ionic energy is understood the potential energy which the negative electron as ion possesses with reference to the positive atom. According to the view expressed, sodium chloride is to be regarded as a compound of chlorine with the negative electron of sodium, which is secondarily accompanied by a compound of sodium with its negative electron. Those atoms or radicles which are charged with negative electrons are to be viewed as saturated, whilst the metal ions—not possessing this negative charge—are inactive substances.

The author further divides ions into three groups: (1) *electron ions*, that is, free negative electrons; (2) *atom ions*, that is, positive or negative electrons attached to a component of a chemical compound (H^+ , NH_4^+ , Cl^- , SO_4^{2-}); (3) *molions*, that is, atom ions united to several molecules (hydrates of ions).

J. McC.

Electrolysis of Formic and Oxalic Acids and of Potassium Carbonate. FRANZ SALZER (*Zeit. Elektrochem.*, 1902, 8, 893—903).—When a solution of formic and sulphuric acids is electrolysed with smooth and platinised anodes, a larger *E.M.F.* is required with the former and considerably less oxidation of the formic acid occurs. Similar results were obtained with solutions of formic acid alone and of sodium formate in presence of potassium hydroxide. With a solution of oxalic and sulphuric acids, the *E.M.F.* required for electrolysis is very little higher with a smooth anode than with a platinised one, so long as the current density is small and the concentration of the oxalic acid large. Under these circumstances, practically the whole current is employed in oxidising the oxalic acid. With larger current densities, or smaller concentrations of the oxalic acid, however, oxygen is evolved along with carbon dioxide at the anode, and the *E.M.F.* required is very considerably larger with the

smooth anode. Aqueous and alkaline solutions of oxalic acid behave in much the same way as those of formic acid. These results are similar to those obtained by Foerster and Müller (Abstr., 1902, ii, 640).

Finally, some experiments on the electrolysis of concentrated solutions of potassium carbonate show that potassium percarbonate is most readily formed in neutral solution; the presence of OH ions or of hydrogen carbonate is unfavourable. A platinised anode diminishes the yield considerably, although the *E.M.F.* required is smaller than with a smooth anode.

T. E.

Limits of Combustibility. L. PELET and P. JOMINI (*Bull. Soc. chim.*, 1902, [iii], 27, 1207—1212).—When a combustible substance is allowed to burn in a determinate volume of air until extinction of the flame occurs, the volume of the residual oxygen depends on the nature of the combustible, especially as regards its volatility and the temperature of its flame, and also on the temperature of the surrounding air. The results obtained in such combustions of a variety of substances, elementary and compound, are tabulated in the original.

T. A. H.

Clapeyron-Clausius Equation for the Latent Heat. K. HÄLLSTÉN (*Zeit. physikal. Chem.*, 1902, 42, 369—374).—The equation referred to may be written as follows: $r = p(w - v) + \rho = T.dp/dT(w - v)$, where r is the latent heat, $p(w - v)$ the external work, and ρ the internal work. Hence if $\rho/wv = x$, it follows that $x = T.dp/dT - p$. This pressure x is identical with the so-called internal pressure, and varies with the temperature, remaining constant, however, during the change from one state of aggregation to another. Using the data obtained by Regnault and others for water, ether, alcohol, acetone, chloroform, carbon tetrachloride, carbon disulphide, and mercury, it is shown that for the change liquid \rightarrow vapour x is greater than p , the external pressure, but that the ratio x/p decreases slowly as the temperature rises. Similar calculations have been made with the data for the freezing points of mercury, lead, and water, x in these cases being of the order 10000—100000 atmospheres.

J. C. P.

Latent Heat of Evaporation of Mercury. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 659—665).—The latent heat of evaporation of mercury was determined by the method of mixtures carried out in a specially devised apparatus. The mean result of four experiments, in which the rise of temperature obtained was about 3.5° and the

quantity of mercury evaporated about 150 grams, is: $\int_{20}^{350} c.dt + \rho = 80.5$.

Measurements were also made of the specific heat of mercury between 340° and 20°, the mean value obtained being 0.03730. Hence the latent heat of evaporation = 67.8 cal.

Trounton's constant (atomic wt. \times latent heat \div absolute boiling

point) has the value 21.5, which shows that liquid mercury is not associated at the boiling point.

Making use of the known boiling point curves of mercury, the Clausius-Clapeyron formula gives : $dp/dt = 0.017194$, from which the density of saturated mercury vapour with reference to that of hydrogen has the approximately theoretical value 100.3. These results are in accord with the supposed high critical temperature of mercury.

T. H. P.

Heat of Solution. ADOLFO VARALI-THEVENET (*Nuovo Cim.*, 1902, [v], 4, 186—192).—By Staub's method, using a Bunsen ice calorimeter, the author has made measurements of the heat absorbed on dissolving varying amounts of potassium and sodium nitrates, chlorides, and sulphates in water. The numbers obtained are compared with those given by other investigators.

The results show that, for not very dilute solutions, an increase in the concentration is accompanied by an almost exactly proportional diminution in the quantity of heat absorbed in the dissolution of a definite amount of salt, whilst in the case of dilute solutions the heat absorbed diminishes more rapidly than the dilution. Further, for salts containing radicles of equal atomicity, there exists a constant relation between the molecular weight and the quantity of heat absorbed for infinitely dilute solutions. Estimating the latter by extrapolation, it is found that the ratios to them of the corresponding molecular weights have the values : for potassium or sodium nitrate, 1 ; for potassium chloride, 0.92 ; for sodium chloride, 1.38 ; for potassium sulphate, 2.14 ; and for sodium sulphate, 2.29.

T. H. P.

Lowering of the Freezing Point of Aqueous Hydrogen Peroxide produced by certain Salts and Acids. HARRY C. JONES and CHARLES G. CARROLL (*Amer. Chem. J.*, 1902, 28, 284—291).—It was previously observed by Jones, Barnes, and Hyde (*Abstr.*, 1902, ii, 203) that potassium chloride, sodium nitrate, and potassium nitrate lower the freezing point of aqueous hydrogen peroxide less than they do that of water. The observed lowerings cannot be interpreted by supposing that aqueous hydrogen peroxide has less dissociating power than water. Experiments of Bredig (*Zeit. Elektrochem.*, 1901, 7, 622) and of Calvert (*Abstr.*, 1902, ii, 11), indicate that hydrogen peroxide acts like a weak acid and can form definite compounds with strong alkalis.

The freezing point determinations of Jones, Barnes, and Hyde were confirmed with potassium chloride and nitrate respectively. Experiments were also made with solutions of ammonium sulphate in water and in hydrogen peroxide. The lowerings observed, more particularly those with potassium nitrate, do not warrant the assumption that the salt molecules had been polymerised or that their dissociation had been diminished by the hydrogen peroxide. The probable explanation is that the molecules of the individual salts combined with the molecules of the peroxide (compare Tanatar, *Abstr.*, 1902, ii, 11). Preliminary experiments on the molecular lowerings produced by sulphuric acid and oxalic acid in water and hydrogen peroxide respectively, indicate

that those acids are more largely dissociated by the peroxide than by water. A. McK.

Critical States of a Binary System. PAUL SAUREL (*J. Physical Chem.*, 1902, 6, 629—635).—A mathematical paper, in which a simple demonstration is given of Gibbs's conditions for the critical state in a binary system. L. M. J.

Pycnometers. ROBERT LEIMBACH (*J. pr. Chem.*, 1902, [ii], 66, 475—477).—The author describes two new pycnometers, which are intended to simplify the operation of filling. G. Y.

Significance of Changing Atomic Volume. III. THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1902, 42, 129—154. Compare Abstr., 1902, ii, 305).—The relations between changes in the heat capacity, changes in the free energy, changes in volume, heat of reaction, and chemical affinity are discussed, and it is shown that these relationships are adequately interpreted with the help of the hypothesis of compressible atoms. J. C. P.

New Determinations of the Surface Tension of Liquids, based on the Capillary Wave Method. LEO GRUNMACH (*Ann. Physik*, 1902, [iv], 9, 1261—1285).—The following values of the tension at a fresh surface were found: pure mercury, 0.50 gram/cm. at 18°; pure distilled water, 0.077 gram/cm. at 17°; absolute alcohol, 0.019 gram/cm. at 22.8°. The effect of leaving the surface exposed to air has been traced; in the case of mercury, prolonged exposure to air lowers the value of the surface tension to 0.33.

The surface tensions of sulphuric acid solutions and of certain oils have also been determined. J. C. P.

Surface Tension of Mixtures of Normal Liquids. EDOUARD HERZEN (*Arch. Sci. phys. Nat.*, [iv], 1902, 14, 232—260).—The values of the surface tension of mixtures of normal liquids are usually not equal to those calculated by means of a simple mixture formula. The author has attempted to show that the variations are due to the variations of internal attraction in the mixtures. The value of the Van der Waals' constant a is given by (1) the expression $\gamma(M/d)^{\frac{2}{3}}M/d$ where γ is the surface tension. The value of a is also (2) equal to $a_1x^2 + 2a_{12}x(1-x) + a_2(1-x)^2$ where a_1 , a_2 are values in the case of the pure liquids, and a_{12} a constant dependent on the influence on one another of the different molecules. The author shows that the values for a_x obtained experimentally as in (1) agree well with those calculated by (2), the values of a_{12} being calculated from the means. The mixtures examined were aniline and toluene, dimethylaniline and toluene, benzene and ethyl acetate, nitrobenzene and ethyl acetate, dimethylaniline and ethyl acetate, aniline and benzene, toluene and *o*-toluidine, toluene and nitrobenzene, benzene and nitrobenzene, aniline and *o*-toluidine, benzene and dimethyl-*o*-toluidine, toluene and dimethyl-*o*-toluidine, aniline and dimethylaniline. L. M. J.

Relation between Negative Pressure and Osmotic Pressure. GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1902, 42, 353—368).—A summary is given of the work done by Berthelot, O. Reynolds, Worthington, Askenasy and others on negative pressure. Experiments are described in which a tube two metres long, closed at one end by a porous porcelain plate containing a semipermeable membrane, was filled with air-free water and inverted, with the porcelain plate uppermost, in a mercury trough. Evaporation of the water took place through the porcelain plate, and the mercury rose to a height much exceeding the atmospheric pressure (in one case to 111.1 cm.) before the water broke away from the under side of the plate. It was further observed that the rate of evaporation diminished as the mercury column rose; in other words, the vapour pressure fell as the negative pressure increased. The author draws attention to the analogy between negative pressure and osmotic pressure, and on the ground of this conception of osmotic pressure as a negative pressure on the solvent deduces the formula $P = -V\Delta p/\phi(d-g)$, where P is the osmotic pressure, ϕ the molecular volume of water, d the weight of solution per c.c., and g the weight of dissolved substance per c.c.; V is the molecular volume of water vapour, and Δp is the change in vapour pressure.

J. C. P.

Molecular Surface-energy of some Mixtures of Liquids. Sir WILLIAM RAMSAY and Miss EMILY ASTON (*Trans. Roy. Irish Acad.*, 1902, 32, 93—100. Compare *Abstr.*, 1895, ii, 40).—The molecular surface-energy of mixtures containing from 10—20 per cent. of one liquid up to 80 or 90 per cent. was determined by the capillarity method (Ramsay and Shields, *Trans.*, 1893, 63, 1089), the following liquids being employed: carbon disulphide and chloroform, ethylene bromide and chlorobenzene, toluene and acetic acid, ethylene bromide and acetic acid, ethyl alcohol and benzene, and ethyl alcohol and chloroform. No definite conclusions are drawn from the results, although it appears that in these cases the molecules are not evenly distributed over the surface. The addition of a non-dissociated substance to a dissociable one does not result merely in the increased dissociation of the latter.

J. McC.

Deduction of the Magnitude of the Osmotic Pressures in Dilute Solutions according to the Kinetic Theory. PETER FIREMAN (*J. Physical Chem.*, 1902, 6, 636—639).—The molecular kinetic energy of both solute and solvent is solely dependent on temperature, and equal to that of a gas at the same temperature. The presence of the solvent will not affect the number of impacts per unit surface of the solute, so that this number will be that obtaining in the case of a gas at the same concentration and temperature. It follows that the osmotic pressure due to the solute is equal to the corresponding gas pressure. Conversely, if the latter is regarded as experimentally proved, it would be deduced that the kinetic energy of the molecules of a liquid is equal to that of gas molecules at the same temperature.

L. M. J.

Composition of the Hydrates of Gases. ROBERT DE FORCRAND (*Compt. rend.*, 1902, 135, 959—961. Compare Abstr., 1902, ii, 392, 446).—By applying the formula previously developed, $Q/T = 30$, where Q is the heat of formation and T is the temperature, the following probable compositions of gas hydrates have been calculated: A, 4 or 5H₂O, CH₄, 6H₂O, CO₂, 6H₂O, N₂O, 6H₂O, C₂H₆, 7H₂O, C₂H₂, 6H₂O, C₃H₄, 7H₂O, PH₃, 6H₂O, H₂S, 6H₂O, C₂H₅F, 8H₂O, SO₂, 8H₂O, CH₃Cl, 7H₂O, H₂Se, 6H₂O, Cl₂, 7H₂O, and Br₂, 10H₂O.

It may be noted that the majority of these contain 6H₂O for one molecule of gas and the quantity of water appears more or less to increase with decreasing volatility of the gases. The compounds are the more stable the more water they contain. J. McC.

Constitution of certain Organic Salts of Nickel and Cobalt as they exist in Aqueous Solution. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1902, 24, 1012—1023).—The molecular conductivities of solutions of the tartrates, malates, and succinates of nickel, cobalt, magnesium, manganese, and barium, and the depression of the freezing point of water caused by the dissolution of these, have been determined. In the more concentrated solutions, the results give higher molecular weights than those calculated from the formula, except for nickel and cobalt tartrates, and, in a less degree, the malates. The molecular conductivity of the tartrates of magnesium, barium, and manganese do not vary very much from each other, but the conductivities of nickel and cobalt tartrates are of an entirely different order. The explanation offered is that the solution contains double molecules as well as complex ions. The presence of hydroxyl groups is not the conditioning factor of the polymerisation, because tartronates give normal results as compared with the malonates, both in conductivity and osmotic experiments.

In connection with these results, attention is called to the influence of hydroxyl groups in increasing the affinity constant of succinic acid; this change is apparent when malic and tartaric acids are examined, but is not noticed when we pass from malonic to tartronic acid. J. McC.

Velocity of Reaction between Potassium Permanganate and Oxalic Acid. RICHARD EHRENFELD (*Zeit. anorg. Chem.*, 1902, 33, 117—128).—It has been proved that reaction takes place quantitatively between potassium permanganate and oxalic acid, in absence of mineral acid, according to the equation: $8C_2H_2O_4 + 2KMnO_4 = 2MnC_2O_4 + K_2C_2O_4 + 10CO_2 + 8H_2O$. The velocity of the reaction was measured by mixing the substances in solution and after a definite time adding a dilute sulphuric acid solution of potassium iodide; the liberated iodine was estimated, and from it the amount of permanganate which had been used was deduced. A fairly satisfactory constant was obtained, but this could be improved by adding previously to the solution either potassium oxalate or manganous oxalate. The reaction is unimolecular.

It is shown that it is the undissociated potassium permanganate which carries out the reaction. The effect of the addition of mineral acid is to increase the pressure of the free positive electricity

($\text{MnO}_4' \rightleftharpoons \text{MnO}_2 + 2\text{O}'' + 3'$; $\text{MnO}_4' \rightleftharpoons \text{MnO} + 3\text{O}'' + 5'$) and so intensify the oxidising power. J. McC.

General Theory of the Action of certain Diastases. VICTOR HENRI (*Compt. rend.*, 1902, 135, 916—919. Compare Abstr., 1902, ii, 127).—It has been shown (*loc. cit.*) that in the decomposition of sucrose by invertase, of salicin by emulsin, and of starch by amylase, the course of the reaction differs markedly from that induced by acids. According to Bodenstein, this difference is due to the depressing influence exerted both by (for example) sucrose, and still more by invert sugar, on the ferment; if this influence is taken into account, a velocity coefficient of constant value is given by a logarithmic formula. With very dilute solutions, however, the author finds that this is not the case. It is suggested, on the other hand, that part of the ferment is combined with the substance to be hydrolysed, part with the product of hydrolysis, and part remains free. Either the latter is the active hydrolytic agent, or the compound of the ferment with the substance to be hydrolysed breaks up into the products of hydrolysis and the ferment. Both hypotheses lead to the same equation for the velocity of reaction. The velocity coefficient calculated in this manner from measurements made with invertase and emulsin has a constant value.

K. J. P. O.

Phase Rule. JACOBUS H. VAN'T HOFF (*Ber.*, 1902, 35, 4252—4264).—A lecture of a general character delivered before the German Chemical Society, dealing with the phase rule and its application to particular cases. J. C. P.

A Representation in Space of the Regions in which Solid Phases occur. H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 279—283).—Photographs are given of the solid representation of the equilibrium in a binary system. The solid enables the exact composition and condition to be read off at any temperature and pressure and indicates the changes the system undergoes by alteration of temperature, pressure, or concentration.

L. M. J.

Equilibria of Phases in the System Acetaldehyde—Paracetaldehyde, with and without Molecular Transformation. H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 283—288).—If a system contains isomeric molecules which can pass into one another, then, if the velocity of molecular change is small, the system on being treated rapidly will behave like one with more components than it shows if treated more slowly. The system acetaldehyde—paracetaldehyde has been studied by the author, the isomeric change only proceeding in the presence of a small quantity of a catalyst, preferably an acid. Without this addition, the freezing point curve passes from 12.55° paracetaldehyde to -118.45° acetaldehyde, with a eutectic point at -119.9° with 1.4 per cent. paracetaldehyde. The boiling

point curve is convex below, passing from 20.7° to 123.7° , the vapour composition curve being widely separated from it. Thus, at 41.7° , the liquid contains 53.7 per cent. paracetaldehyde, but the vapour only 2.5 per cent. The critical temperature curve extends from 188 — 286° . In the presence of a trace of acid, the boiling point of all mixtures soon reaches 41.7° , where the composition of the liquid and vapour is as stated above, so that the point indicates the equilibrium for 41.7° and 1 atmosphere. By lowering of temperature, the equilibrium is displaced, and at 6.8° the melting point curve is reached, the percentage of paracetaldehyde being 88.1. The critical curve is reached at 221° , at which temperature liquid and vapour contain 11 per cent. of paracetaldehyde. The form of the spacial representation is briefly considered.

L. M. J.

Equilibrium between Carbamide and Ammonium Cyanate.

JAMES WALKER (*Zeit. physikal. Chem.*, 1902, 42, 207—208).—The author points out that the results obtained in his laboratory (Walker and Hambly, *Trans.*, 1895, 67, 746; Walker and Kay, *Trans.*, 1897, 71, 507; Walker and Wood, *Trans.*, 1900, 77, 28) are in no way inconsistent with Fawsitt's observations (this vol., ii, 15) on the displacement of the equilibrium with rise of temperature. On the contrary, when the author's value for the heat effect accompanying the transition of cyanate into carbamide and Fawsitt's value for the equilibrium constant at 90° are inserted in van't Hoff's equation, the equilibrium constant at 99° can be calculated in close agreement with experiment.

J. C. P.

Equilibrium Phenomena in Precipitation Reactions. III. The Precipitation of Mixed Bromide and Thiocyanate Solutions by Silver. FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1902, 33, 129—139. Compare *Abstr.*, 1899, ii, 205; 1900, ii, 255, 521).—The composition of the precipitate formed by adding silver nitrate solution to a mixed solution of potassium bromide and thiocyanate was determined by heating in a Rose crucible in a current of chlorine and weighing as silver chloride.

The results are graphically represented; the molecular percentages of silver bromide in the precipitate are taken as abscissæ, whilst the ordinates are the molecular percentages of potassium bromide in the solution. Silver bromide and silver thiocyanate are only partially miscible. Silver thiocyanate takes up only about 3 per cent. of silver bromide, and if more is added a saturated solution of silver thiocyanate (10 per cent.) in silver bromide is formed.

The solubility of the precipitates was measured by determination of the potential as before (*loc. cit.*). The results obtained indicate that the silver ion concentration multiplied by the bromine ion concentration is smaller than the solubility product of silver bromide (65.3×10^{-14}), and therefore the solubility of the silver bromide has been diminished by isomorphous admixture with silver thiocyanate. The solubility of silver thiocyanate is calculated to be 1.08×10^{-6} .

J. McC.

Intramolecular Rearrangement of Atoms in Halogen-acetanilides [Acetylphenylchloroamines] and its Velocity. II. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5 359—362. Compare Abstr., 1902, ii, 646).—The change which acetylphenylchloroamine undergoes in acetic acid in presence of hydrochloric acid proceeds as a unimolecular reaction. The velocity of reaction both in alcoholic and acetic acid solution is decreased by addition of water; the velocity increases with increasing concentration of the hydrochloric acid, and would apparently be zero in absence of this acid. The velocity is greater in acetic acid solution than in alcohol.

J. McC.

Transition of Polymorphous Substances. JULIUS MEYER (*Zeit. anorg. Chem.*, 1902, 33, 140—148).—The author develops the following relationship: $\log \frac{C_a}{C_b} = \frac{Q}{2} \left(\frac{1}{\delta} - \frac{1}{T} \right)$, where C_a and C_b are the solubilities of two different forms of a substance, Q is the heat of transition (equal to $Q_a - Q_b$, the heats of solution), and δ is the transition temperature. The solubility of specially prepared rhombic sulphur was determined at 25.1° and 13.3° in chloroform, benzene, and ether. The solubility of monoclinic sulphur was determined at the same temperatures by saturating the solvents with rhombic sulphur and allowing the monoclinic variety to crystallise out at the right temperature.

The solubility quotient, $C_{rh.}/C_{m.}$, is approximately constant; at 25.1°, in chloroform, it is 0.9954; in benzene, 0.9949; and in ether, 0.9961; at 13.3°, it is 0.9925 in chloroform; in benzene, 0.9971; and in ether, 0.9992. The monoclinic sulphur is therefore more soluble than the rhombic, and the ratio of the solubilities is constant at constant temperature and independent of the nature of the solvent. The natural logarithm of the solubility quotient agrees with that calculated by means of the above formula from the heat of transition.

J. McC.

Nature of Liquid Crystals. RUDOLF SCHENCK (*Ann. Physik*, 1902, [iv], 9, 1053—1060. Compare Abstr., 1898, ii, 286, 563; 1899, ii, 360, 637; 1900, ii, 339).—The author criticises Tammann's work (Abstr., 1901, ii, 231; 1902, ii, 445), and argues against the emulsion theory. Further evidence in favour of the existence of crystalline liquids is found in the fact that the intensity of turbidity in the case of *p*-azoxyanisole, as measured by the absorption, does not increase with falling temperature; this would certainly be the case if the emulsion theory were the correct one. Stress is also laid on the fact that there is a discontinuity both in the viscosity and in the density at the point where the turbid crystalline liquid becomes clear and non-crystalline.

Reference is made to ethyl *p*-azoxybenzoate, which has been found to melt at 113.5° to a turbid liquid, exhibiting the usual characteristics of crystalline liquids, and becoming clear at 120.5°.

J. C. P.

Effects of Strain on the Crystalline Structure of Lead. J. C. W. HUMFREY (*Phil. Trans.*, 1902, 200, 225—240).—Large crystals of lead were produced by slowly cooling the molten metal

from the top and pouring off the residual liquid after partial solidification had taken place. The etch-figures, produced by 5 per cent. nitric acid, are of a cubo-octahedral form. When the crystal is strained in tension, elongation takes place, due to numerous slips along the gliding planes of the crystal. The strained crystals were etched and the slip planes oriented by their relation to the etch-figures. Lead tends to slip along planes perpendicular to the octahedral axes of the crystals. Some slight differences of orientation of the slip lines occurred after a single crystal had been strained, but this is not due to recrystallisation, but to the fact that the strain was not homogeneous; when a slip has occurred in a certain part, it tends to go on there rather than in other parts of the specimen. After straining, the lead recrystallises, and it has been proved that the recrystallisation is not a direct and instantaneous effect of the strain, but severe strain and high temperature both tend to increase the subsequent rate of change of structure. The patches of new orientation probably start from a cleavage plane, and this gives rise to the formation of twin crystals, the occurrence of which has been very frequently observed.

J. McC.

New Controllable Apparatus for Heating Sealed Tubes. ALFRED JUNGHAHN (*Chem. Zeit.*, 1902, 26, 1176—1177).—A furnace is described (with a figure) in which a sealed tube can be heated, and at the same time observed, without removal from the apparatus. An arrangement is also fitted by means of which the tube can be partially withdrawn from the mantle and thus opened with safety.

K. J. P. O.

Inorganic Chemistry.

Amount of Free Hydrogen in the Air and the Density of Atmospheric Nitrogen. ARMAND GAUTIER (*Compt. rend.*, 1902, 135, 1025—1032).—The author discusses the observations of Leduc, Rayleigh, himself, and earlier observers on the densities of the air and its constituents, and on the amount of hydrogen in the air. Whilst hydrogen seems to be always present in the air, its proportion varies considerably. The presence of hydrogen affects the accuracy of the older determinations of the proportion of nitrogen in the air, and its variable amount affords an additional reason against the use of air as a standard for the density of gases.

C. H. B.

Reaction of Iodine with Mercuric Oxide in Presence of Water. ROBERT L. TAYLOR (*Mem. Manchester Phil. Soc.*, 1902, 1, [i], 1—6. Compare Abstr., 1897, ii, 207; and Proc., 1902, 18, 72).—The reason why Orton and Blackman (*Trans.*, 1900, 77, 835) obtained

such a small quantity of hypiodite was that their experiments extended over too long a period, and the hypiodite had time to decompose. The author's previous experiments have been confirmed. Using precipitated iodine, the amount of hypiodous acid present amounts to about 50 per cent. of that possible according to the equation $\text{HgO} + 2\text{I}_2 + \text{H}_2\text{O} = \text{HgI}_2 + 2\text{HOI}$, whilst with iodine in solution, the yield varies from 90 to 95 per cent. J. McC.

Amorphous Sulphur and its Relation to the Freezing Point of Liquid Sulphur. ALEXANDER SMITH (*Proc. Roy. Soc. Edin.*, 1902, 24, 299—301).—Amorphous sulphur is formed by heating liquid sulphur, in increasing proportion as the temperature is raised. It is shown that specimens of liquid sulphur which have been thus heated solidify at a temperature below the freezing point of pure soluble sulphur, the depression being proportional to the amount of amorphous sulphur which has been formed. Investigation of samples containing from 0.76—3.72 grams of amorphous sulphur per 100 grams of soluble sulphur has given 42.6° as the mean value of the atomic depression. The molecular depression, calculated by van't Hoff's formula, is 325, whence it seems that the molecule of amorphous sulphur contains eight atoms. Soluble sulphur has been shown to have the formula S_8 in solution, and it is therefore probable that the change taking place when liquid sulphur is heated consists in an intramolecular rearrangement. J. C. P.

Causes which Determine the Formation of Amorphous Sulphur. ALEXANDER SMITH (*Proc. Roy. Soc. Edin.*, 1902, 24, 342—343).—The quantities of amorphous sulphur formed on heating liquid sulphur to various temperatures from 130 — 448° vary in an irregular manner, and investigation shows that foreign substances, for the most part without chemical action on sulphur, exert a great influence on the production of the amorphous form. This production is favoured by passing dry air, sulphur dioxide, or dry hydrogen chloride through the liquid sulphur or by adding glacial phosphoric acid; it is hindered by nitrogen, carbon dioxide, hydrogen sulphide, or ammonia. These gases also reduced the quantity to the same minima when, by use of air or sulphur dioxide, the larger amounts had already been formed. In the case of phosphoric acid, however, treatment with carbon dioxide does not reduce the proportion, presumably because this acid is non-volatile. Conversely, air and sulphur dioxide restore the amorphous sulphur, which has been destroyed by treatment with carbon dioxide. It is inferred that absolutely pure sulphur would not form any amorphous sulphur on heating (compare Malus, *Abstr.*, 1902, ii, 131). J. C. P.

Transformation of Pyrophosphoric into Orthophosphoric Acid. H. GIRAN (*Compt. rend.*, 1902, 135, 961—963. Compare *Abstr.*, 1902, ii, 549).—By maintaining syrupy pyrophosphoric acid at about -10° for three months, it was obtained in the form of white needles which melt at 61° . The crystallisation is exceedingly slow. The heat of solution of the crystallised acid was found to be 7.93 Cal. The heat of fusion, determined from the difference of the heats

of solution of the solid and of the liquid, is -2.29 Cal. The heat of solution of orthophosphoric acid obtained from the solid pyrophosphoric acid was determined and the following deduced from the result: $\text{H}_4\text{P}_2\text{O}_7$ (solid) + aq. = $2\text{H}_3\text{PO}_4$, aq. + 6.97 Cal.; $\text{H}_4\text{P}_2\text{O}_7$ (liquid) + aq. = $2\text{H}_3\text{PO}_4$ aq. + 9.09 Cal.; $\text{H}_4\text{P}_2\text{O}_7$ aq. = $2\text{H}_3\text{PO}_4$ aq. + 4.25 Cal.; $[\text{H}_4 + \text{P}_2 + \text{O}_7] = \text{H}_4\text{P}_2\text{O}_7$ (solid) + 532.23 Cal. J. McC.

The Diffusion of Arsenic in Nature. F. GARRIGOU (*Compt. rend.*, 1902, 135, 1113—1115. Compare Bertrand, this vol., ii, 91, and Gautier, *ibid.*).—The method adopted for recognising the presence of very small quantities of arsenic is as follows: the powdered substance is evaporated nearly to dryness with pure *aqua regia* three times, then three or four times with pure hydrochloric acid to expel the nitric acid. The residue is dissolved in dilute hydrochloric acid, filtered, and a current of sulphur dioxide passed through for an hour. The dissolved sulphur dioxide is expelled by heating and a current of hydrogen sulphide is then passed through the solution for 50 hours. The liquid is digested at 40° for 50 hours and a current of hydrogen sulphide again passed through for 12 hours. After settling, the clear liquor is decanted off and the precipitate washed with boiling water. The precipitate is treated with ammonia, which dissolves the arsenious sulphide, and the residue obtained by evaporating the solution is examined in the flame. In this way, the presence of $1/100000$ mg. of arsenic can be detected.

Experiments extending over thirty years have shown the presence of arsenic in all the rocks and metalliferous deposits examined; crystalline minerals are apparently free from it. All mineral and potable waters investigated contain arsenic, which has also been found in all plant ashes and in wine. It has been detected too in 12 poisoning cases, where compounds of copper, zinc, mercury, or potassium cyanide were the poisoning agents. The author regards arsenic as one of the most widely distributed elements in nature.

J. McC.

Diffusion of Arsenic in Nature. ARMAND GAUTIER (*Compt. rend.*, 1902, 135, 1115. Compare preceding abstract).—The assumption that arsenic is distributed throughout the various organs of animals is incorrect. It is only found in the skin and in glands near the skin. In these researches, care must be taken that the reagents and the glass do not contain arsenic; Jena glass contains an appreciable amount of this element.

J. McC.

Action of Sodium Ortharsenite on the Solutions of Salts of Metals. C. REICHARD (*Chem. Zeit.*, 1902, 26, 1141—1145).—The preparation and properties of the following salts are described: $5\text{CuO}, \text{As}_2\text{O}_3$; $3\text{HgO}, \text{As}_2\text{O}_3$; $3\text{Hg}_2\text{O}, \text{As}_2\text{O}_3$; $3\text{Ag}_2\text{O}, \text{As}_2\text{O}_3$; $2\text{Ag}_2\text{O}, \text{As}_2\text{O}_3, 4\text{NH}_3$; $14\text{NiO}, \text{As}_2\text{O}_3$; $7\text{CoO}, \text{As}_2\text{O}_3$; and $5\text{CdO}, \text{As}_2\text{O}_3$.

K. J. P. O.

Action of Ammonia on Boron Chloride. ALEXANDRE JOANNIS (*Compt. rend.*, 1902, 135, 1106—1109).—A current of hydrogen

carrying with it boron chloride vapour was passed through liquid ammonia kept at between -70° and -50° . The temperature of the product was then raised to -23° and the excess of ammonia volatilised. At this temperature, 1 mol. of boron chloride fixes 15 mols. of ammonia; when the temperature is raised to 0° , 9 mols. of ammonia are expelled, and the vapour tension during this loss of ammonia is the same as that of the additive compound $\text{NH}_4\text{Cl}, 3\text{NH}_3$. During the reaction, no hydrogen or nitrogen is evolved (that no hydrogen is produced was proved by carrying out the experiment with a current of air), and from the increase in weight and the action of water on the product, whereby boric acid is formed, it is found that for the three ammonium groups formed three amino-groups are produced which are united to the boron. The reaction at -23° is: $\text{BCl}_3 + 15\text{NH}_3 = 3(\text{NH}_4\text{Cl}, 3\text{NH}_3) + \text{B}(\text{NH}_2)_3$; and at 0° : $\text{BCl}_3 + 6\text{NH}_3 = 3\text{NH}_4\text{Cl} + \text{B}(\text{NH}_2)_3$. When boramide is heated to 440° , it loses 1.5NH_3 and is converted into borimide: $2\text{B}(\text{NH}_2)_3 = 3\text{NH}_3 + \text{B}_2(\text{NH})_3$. This decomposition, although slow, begins at the ordinary temperature, consequently the reaction of ammonia on boron chloride at the ordinary temperature is complicated, and this explains why varying results have been obtained.

It has not been possible to completely separate the boramide from the ammonium chloride, although the latter is more soluble in liquid ammonia, but the borimide can be easily obtained free from ammonium chloride by washing with liquid ammonia.

It is probable that the products obtained by the action of ammonia on boron sulphide, bromide, and iodide are not additive compounds, but mixtures of ammonium salt with boramide. J. McC.

Temperature of Inflammation and the Combustion of Three Varieties of Carbon in Oxygen. HENRI MOISSAN (*Compt. rend.*, 1902, 135, 921—928).—Diamond was heated in a porcelain tube with glass ends in a current of oxygen, and the gas was passed into a solution of barium hydroxide. The temperature was measured by a Le Chatelier thermo-electric couple; at 710° , there was no evidence of the formation of carbon dioxide after heating for 15 minutes, but at 720° a distinct turbidity appeared in the baryta solution. The amount of carbon dioxide formed increased with rise of temperature, and at 790° the formation was abundant. When the temperature reached 800° , the diamond became incandescent and surrounded by a flame. This has been repeated with other diamonds and the inflammation temperature has always been found to lie between 800° and 850° . The combustion proceeds quickly at a temperature 20° below the point of inflammation. The diamond does not depolymerise during the active combustion.

The point of inflammation of graphite, artificially prepared by the action of silicon on fused iron rich in carbon, was determined in the same way. At 570° , there was an evident formation of carbon dioxide, which was abundant at 600° , and the graphite inflamed at 690° . Graphite obtained by heating diamond in the electric furnace began to form carbon dioxide at 510° , and its point of inflammation was likewise found to be 690° .

Amorphous wood charcoal was carefully purified and freed from absorbed gases. When it was heated in a current of oxygen at 200° , no appreciable quantity of carbon dioxide was formed. At 230° , the formation of carbon dioxide was observed; as the temperature rose, the production increased and the material inflamed at 345° .

Amorphous carbon was placed with oxygen in sealed tubes. Carbon dioxide was not formed, either when preserved at the ordinary temperature in the dark for a year or when the tubes were exposed to sunlight during September. When the tubes were heated for 300 hours at 50° , no carbon dioxide was formed, but at 100° , after 140 hours, the presence of carbon dioxide was detected. When heated at $104-110^{\circ}$ for 200 hours, about 10 per cent. of the oxygen was converted into carbon dioxide, and at 198° , after 24 hours, half of the oxygen was transformed.

Acetylene black, when heated in a current of oxygen, gave traces of carbon dioxide at 240° and became incandescent at 635° .

The extent of the oxidation depends on the presence of water and on the nature of the surface of the carbon. J. McC.

Artificial Diamonds. RUDOLF VON HASSLINGER (*Monatsh.*, 1902, 23, 817—822).—One to two per cent. of carbon is added to a mixture, the composition of which is close to that of the matrix in which diamonds are found, and the mass fused by the alumino-thermal method. After cooling, the mass is dissolved by ammonium fluoride and sulphuric acid, leaving small, clear, colourless diamonds (diameter 0.05 mm.). The author considers that slower cooling would result in larger diamonds (compare Ludwig, *Abstr.*, 1902, ii, 451). G. Y.

Transformation of Diamond into Charcoal during Oxidation. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1902, 135, 1018—1020).—When the diamond is burnt in oxygen, a small quantity of black, amorphous carbon is formed, seemingly as the result of an isomeric change at the moment of combustion. C. H. B.

Action of an Oxide or a Metallic Hydroxide on the Solutions of Salts of other Metals. Mixed Basic Salts. ANABLE MAILHE (*Ann. Chim. Phys.*, 1902, [vii], 27, 362—397).—A résumé of a series of researches, previously published (*Abstr.*, 1901, ii, 452, 509, 601; 1902, ii, 140, 261). K. J. P. O.

Theory of the Action of Halogens on Alkalis. FRITZ FOERSTER and ERICH MÜLLER (*Zeit. Elektrochem.*, 1902, 8, 921—926).—The fundamental reaction between a halogen (X_2) and a solution containing hydroxyl ions may be written $X_2 + 2OH' = 2X' + H_2O + O$. With the exception of fluorine, the halogens only react in this way in presence of a catalyser such as platinum black or cobalt oxide; otherwise, the reaction stops at an intermediate stage, $X_2 + OH' = X' + XOH$. In presence of excess of OH ions, another equilibrium is also attained: $XOH + OH' = XO' + H_2O$. The concentrations of the different substances are connected by the equations $C_{X_2}/C_{X'} = K_1 C_{XOH}/C_{OH'}$ and $K_2 C_{OX'}/C_{(OH')^2}$. These equilibria can only be realised when the concentrations are such that the further reactions, $2XOH + XO' = XO'_3 +$

$2X' + 2H'$ and $2X' + 2H' + 2XO' = 2XOH + 2X'$, take place very slowly. The authors apply this theory to the action of chlorine on alkali hydroxides and find that although data for the accurate calculation of the equilibrium constants are not yet in existence, the approximate values obtainable agree well with the observed phenomena. T. E.

Action of Alkalis on Glass and on Paraffin. FRANCIS JONES (*Mem. Manchester Phil. Soc.*, 1902, 47, iii, 1—17).—In order to find whether the glass vessel used in Pettenkofer's method of estimating carbon dioxide in air has any influence on the result, the action of lime and baryta water on glass was examined. The results show that lime-water, in contact with the glass of bottles, loses strength much more quickly than baryta water under the same circumstances, and that lime-water combines with silica more rapidly than baryta water. Neither solution exerts any appreciable action on glass bottles in the first few hours, hence the accuracy of the Pettenkofer test cannot be affected. As a matter of fact, the loss of strength of baryta water, even on standing in a glass bottle for six months, was found to be very trifling. A paraffined bottle may safely be used in carrying out the Pettenkofer test, but the storage in paraffined bottles is quite inadmissible, since baryta acts on paraffin to a very marked extent after some time. J. McC.

Potassium Sulphates. WILLEM STORTENBEKER (*Rec. trav. chim.*, 1902, 21, 399—411).—The composition of a salt deposited by a solution containing sulphuric acid and potassium sulphate is dependent upon (a) the mol. ratio H_2SO_4/K_2SO_4 in the solution and (b) the concentration of the solution. When a salt containing 1 mol. each of potassium sulphate and potassium hydrogen sulphate is concentrated, there separates a salt of the composition $K_2SO_3 \cdot KHSO_4$, which crystallises in brilliant, biaxial, monoclinic lamellæ, and has a sp. gr. 2·587 (compare Marignac, *Ann. des Mines*, 1856, 9, 7, and Wyruboff, *Bull. Soc. Min.*, 1880, 3, 209). From dilute solutions containing 1 mol. of the normal sulphate and 2—3 mols. of sulphuric acid, there separates as nacreous, hexagonal lamellæ, the salt $K_2SO_4 \cdot 3KHSO_4$, which has a sp. gr. 2·463, and from solutions more concentrated, but having the same relative amounts of potassium sulphate and sulphuric acid, the salt $K_2SO_4 \cdot 6KHSO_4$, which crystallises in minute needles and has a sp. gr. 2·327 (compare Wyruboff, *Abstr.*, 1886, 665). This has a restricted range of stability and readily changes into either of the more stable salts $K_2SO_4 \cdot 3KHSO_4$ or $KHSO_4$. In the original paper, a diagram is given showing the ranges of stability of these salts.

T. A. H.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXVIII. Artificial Preparation of Kaliborite. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 1008—1012).—Kaliborite, $KMg_2B_{11}O_{19} \cdot 9H_2O$, occurs along with pinnoite and kainite, and is probably formed from pinnoite in contact with a saturated solution of kainite. This view is supported by a dilatometer experiment, and the conditions are thus indicated

under which kaliborite may be obtained. The author has worked out several preparation methods, of which the following is the simplest; it is founded on the observation that kaliborite in water at 100° is only slowly converted into pinnoite, and that the presence of boric acid almost entirely prevents the change.

The acid borate of magnesium, $\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, was prepared by adding magnesium hydroxide to 30 grams of boric acid dissolved in water, and the solution was concentrated to 75 c.c. To this was added another solution containing 3.6 grams of potassium hydroxide and 10 grams of boric acid in 30 c.c. of water. If the mixture was kept at 100° and stirred to prevent the formation of crust, about 13 grams of kaliborite was obtained.

A second potassium magnesium borate may be obtained in the cold from pinnoite and potassium chloride; this borate contains K_2O 13.3 per cent., and is soluble in warm water. J. C. P.

Formation of Oceanic Salt Deposits. XXIX. The Temperature of Formation of "Hartsalz." JACOBUS H. VAN'T HOFF and WILHELM MEYERHOFFER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 1106—1109. Compare Abstr., 1901, ii, 558).—"Hartsalz," a mixture of sylvite, kieserite, and sodium chloride, is a secondary product formed by the action of solutions on a previously formed combination of carnallite, kieserite, and sodium chloride. The temperature of formation of "hartsalz" is the lowest temperature at which kainite splits into kieserite and sylvite, and by heating a mixture of kainite (1 mol.), carnallite (0.23 mol.), and sodium chloride (0.02 mol.) in sealed tubes it was found that the change takes place between 45° and 80° . A dilatometric examination of a mixture of kainite and carnallite showed that the change occurs above 70° , and the exact temperature at which "hartsalz" is formed was found, by means of the tensimeter, to be 72° . J. McC.

Electrolysis of Fused Sodium Hydroxide. RICHARD LORENZ (*Zeit. Elektrochem.*, 1902, 8, 873—874). MAX LE BLANC and JOHANNES BRODE (*ibid.*, 939—940).—Polemical with regard to Le Blanc and Brode's criticisms (this vol., 18) of Sacher's results (Abstr., 1902, ii, 120). T. E.

Sodium Hypochlorite. CH. SUNDER (*Bull. Soc. ind. Mulhouse*, 1902, 27, 255—260).—The presence of sodium hydrogen carbonate in the sodium carbonate employed for the manufacture of sodium hypochlorite by double decomposition with bleaching powder leads to rapid decomposition of the hypochlorite first formed; a similar result is brought about by the addition of ammonium chloride to solutions of sodium hypochlorite, or, more slowly, by the application of heat to the latter. The action of the sodium hydrogen carbonate may be avoided in practice by the addition of calcium hydroxide to the bleaching powder used. Calcium hypochlorite in solution is scarcely affected by the addition of potassium or sodium hydrogen carbonates or by heating to ebullition.

The sodium derivative of phenolphthalein is immediately decolorised

by sodium hypochlorite, so that it is not possible to titrate alkali hydroxides in presence of hypochlorites, using phenolphthalein as an indicator, as suggested by Blattner (*Abstr.*, 1893, ii, 91). T. A. H.

Behaviour of Sodium Sulphate in Aqueous Solution. ARTHUR HANTZSCH (*Zeit. physikal. Chem.*, 1902, 42, 202—206).—According to Wyrouboff (*Abstr.*, 1901, ii, 149), a freshly prepared solution of thenardite behaves differently on precipitation with alcohol from one of fused sodium sulphate. This observation is shown to be incorrect, for if the temperature is the same in the two cases and is not allowed to rise above 32°, analysis proves that crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ separate from both solutions. J. C. P.

Preparation of Metallic Calcium. WILHELM BORCHERS and L. STOCKEM (*Zeit. Elektrochem.*, 1902, 8, 938).—The methods described by Arndt (this vol., ii, 76) and by Ruff and Plato (this vol., 19) are no better than the old Bunsen and Matthiessen process owing to the fact that fused calcium is rapidly dissolved by fused calcium chloride. Good yields can be obtained only when the metal is deposited in the solid form. E.

Formation of Bleaching Powder. F. WINTERER (*Zeit. anorg. Chem.*, 1902, 33, 161—192).—Difficulty has been experienced in the production of bleaching powder from electrolytically prepared chlorine, and this has been traced to the carbon dioxide with which the gas is always contaminated. The author discusses also the presence of carbon dioxide in chlorine prepared by the ordinary methods, and the experiments are directed towards establishing the conditions most favourable for the production of a good bleaching powder.

From a consideration of the work carried out on chlorine water, the author concludes that the balance of evidence is in favour of regarding this as a solution of hydrochloric and hypochlorous acids.

The various theories which have been suggested to explain the formation of bleaching powder are discussed; three points may be mentioned as important in the production of a good bleaching powder: (a) the calcium hydroxide must be as pure as possible, free from other mineral constituents and from carbonate, (b) the excess of water present should not exceed 5 per cent., and (c) the chlorination temperature should not be too low, neither should it exceed 40°; the optimum temperature is about 20°.

The lime used in the experiments was obtained by igniting a pure marble. The marble was heated to redness for 24 hours, then thrown into water, and the granular hydrate thus obtained was again heated to redness. The lime so obtained was incompletely slaked and exposed to the action of chlorine; when 7.4 per cent. of water is present, the bleaching powder formed contains 8.2 per cent. of active chlorine; when there is 12.1 per cent. of water, the product contains 17.2 per cent. of active chlorine. The lime was then completely slaked and the calcium hydroxide dried at 120°. In contact with dry chlorine, no reaction took place, but chlorination started as soon as a drop of water was added, and the temperature rose very considerably. This

indicates that bleaching powder is not formed directly from calcium hydroxide and chlorine, but that an intermediary product with water is formed; the water is essential for the process and plays a catalytic part. It is probable that the chlorine dissolves in the water and the products of hydrolysis then act on the calcium hydroxide. On cooling a concentrated solution of bleaching powder, crystals of calcium hydroxychloride, $\text{Cl}\cdot\text{Ca}\cdot\text{OH}$, separate. These, however, always contain some hypochlorite chlorine which can be removed by washing with calcium chloride solution. Since the hydrochloric acid of the hydrolysed chlorine acts on the calcium hydroxide to produce calcium hydroxychloride, it seems probable that the hypochlorous acid will act in like manner and give rise to calcium hydroxyhypochlorite, $\text{ClO}\cdot\text{Ca}\cdot\text{OH}$. The hypochlorous acid reacts also with the calcium hydroxychloride: it is, indeed, known that by passing hypochlorous acid over calcium hydroxychloride, bleaching powder is formed. Furthermore, hypochlorous acid reacts also on calcium chloride, which is likewise produced by the action of the hydrochloric acid on the calcium hydroxide.

The decomposition of bleaching powder into calcium chloride and oxygen, a change which takes place in alkaline solution at a high temperature, has been studied. This is a condition which prevails in the bleaching powder chambers at the beginning of the process when the chlorine is conducted over moist calcium hydroxide, much heat being developed. The occurrence of free oxygen has actually been established in the manufacture. This decomposition can be prevented by adequate cooling or by using a diluted chlorine. The influence of the hydroxyl concentration has been followed, and it was found that the greater this concentration the greater is the decomposition. Up to a concentration of 10 per cent., sodium hydroxide exercises a preserving influence on the hypochlorite chlorine, then to a concentration of about 35 per cent. the formation of chlorate takes place, but above that only decomposition with evolution of oxygen occurs.

Free hypochlorous acid decomposes with formation of chloric and hydrochloric acids until an equilibrium is established, and if calcium carbonate is added the hypochlorous acid does not act on this, but the hydrochloric acid does, and as the equilibrium is thus disturbed further decomposition of the hypochlorous acid takes place.

When dry carbon dioxide is passed over dry bleaching powder, no diminution in the amount of active chlorine takes place, and if the amount of water present in the calcium hydroxide be such that the velocity of reaction of the chlorine with the water is greater than that of the carbon dioxide with water, bleaching powder can be obtained from chlorine containing carbon dioxide provided that the mixture of gases is dry.

J. McC.

Dicalcium Silicate in Portland Cement. ORAZIO REBUFFAT (*Gazzetta*, 1902, 32, ii, 243—253).—A controversial paper criticising the work of various authors on this subject.

T. H. P.

Action of Cadmium Hydroxide on Ammonium Salts. HERMANN GROSSMANN (*Zeit. anorg. Chem.*, 1902, 33, 149—155. Compare *Abstr.*, 1902, i, 662).—Cadmium hydroxide is dissolved by ammonium

chloride solution, and from the solution there crystallises an additive product of cadmium chloride with ammonia, $\text{CdCl}_2 \cdot 2\text{NH}_3$, and the double salts $\text{NH}_4\text{Cl}, \text{CdCl}_2$ and $4\text{NH}_4\text{Cl}, \text{CdCl}_2$. The last named predominates, and possibly the other is formed from it.

When ammonium bromide solution is saturated with cadmium hydroxide, the compound $\text{CdBr}_2 \cdot 2\text{NH}_3$ first crystallises out. Ammonium bromide then separates, and then the double salt $\text{CdBr}_2 \cdot 4\text{NH}_4\text{Br}$, which crystallises in monoclinic, rhombohedral prisms. The mother liquor deposits crystals of the double salt $\text{CdBr}_2 \cdot \text{NH}_4\text{Br} \cdot \frac{1}{2}\text{H}_2\text{O}$.

With ammonium iodide solution, the ammonia additive product $\text{CdI}_2 \cdot 2\text{NH}_3$, was obtained, and the double salt $\text{CdI}_2 \cdot \text{NH}_4\text{I} \cdot \text{H}_2\text{O}$.

J. McC.

Supposed Transition Point of the Hydrate of Cadmium Sulphate, $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$. H. VON STEINWEHR (*Ann. Physik*, 1902, [iv], 9, 1046—1052).—The irregular behaviour of the Weston cell (compare Jaeger and Wachsmuth, *Abstr.*, 1897, ii, 86; Jaeger, *Abstr.*, 1898, ii, 364; Cohen, *Abstr.*, 1900, ii, 702; 1901, ii, 142; Jaeger and Lindeck, *Abstr.*, 1900, ii, 703; 1901, ii, 368; Wind, *Abstr.*, 1901, ii, 368; Bijl, this vol., ii, 6) has been attributed by Kohnstamm and Cohen (*Abstr.*, 1898, ii, 495) partly to a change undergone by cadmium sulphate at 15° , experimental evidence of this change being obtained from the solubility curve. The author has accurately determined the solubility of cadmium sulphate from 13.7 — 25° , and finds no evidence in favour of the view that cadmium sulphate has a transition point at 15° .

J. C. P.

Thallic Chloride. VICTOR THOMAS (*Compt. rend.*, 1902, 135, 1051—1054. Compare *Abstr.*, 1902, ii, 322, 658).—Thallic chloride, $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$, forms long, transparent needles and melts at 36 — 37° . At 17° , it is not deliquescent unless the hygrometric condition of the atmosphere is higher than 63 per cent.; at this temperature, 86.2 parts dissolve in 100 parts of water, and the saturated solution has a sp. gr. of 1.85. If the hydrated chloride is enclosed in a vacuum with some sodium hydroxide contained in a separate vessel, the chloride first melts more or less completely, rapidly losing water, and yielding the anhydrous chloride in large, hexagonal crystals which melt at about 25° , dissolve in most solvents, and rapidly become hydrated in contact with moist air. Dehydration in a vacuum is not accompanied by any loss of chlorine. Since, however, the compounds $\text{TiCl}_2\text{Br} \cdot 4\text{H}_2\text{O}$ and $\text{TiClBr}_2 \cdot 4\text{H}_2\text{O}$, previously described (*loc. cit.*), lose both chlorine and bromine in a vacuum, they cannot be regarded as compounds of thallic chloride with thallic bromide.

C. H. B.

Solubility of Red and Yellow Mercuric Oxide and its Dissociation. KARL SCHICK (*Zeit. physikal. Chem.*, 1902, 42, 155—173).—At 25° , a litre of pure water dissolves 0.0518 gram of yellow mercuric oxide and 0.0513 gram of the red oxide; at 100° , the corresponding quantities dissolved are 0.41 and 0.38 gram. The amount of dissolved oxide was determined both by evaporation and by titration with standard acid after addition of sodium chloride in excess. The author regards his experiments as strongly supporting Ostwald's

view (Abstr., 1900, ii, 712; compare also Hulett, Abstr., 1901, ii, 493), that the red and yellow oxides differ only in their state of division and are not isomeric (compare Cohen, Abstr., 1900, ii, 184, 381).

The solubility of mercuric oxide is increased in the presence of OH' ions, and it is probable that a salt is formed in which the mercury is part of a complex anion.

Prolonged action of mercuric oxide solution on ethyl acetate at 25° did not cause the least trace of hydrolysis. From this, and also from the fact that the conductivity of mercuric oxide solutions is only slightly greater than that of pure water, it follows that the degree of dissociation in these solutions is extremely small. On the other hand, when alkali chloride is added to mercuric oxide solutions, there is a formation of mercuric chloride or allied complex compounds, and, consequently, a formation of OH' ions. Thus, ethyl acetate is hydrolysed by a solution containing both mercuric oxide and sodium chloride, but not by a solution containing either alone.

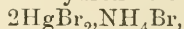
The tint of yellow mercuric oxide varies with the temperature; as the latter rises, it gradually becomes red. J. C. P.

Decomposition of Mercurammonium Salts by Heat. JATINDRANATH SEN (*Zeit. anorg. Chem.*, 1902, 33, 197—208).—"Infusible white precipitate," NH_2HgCl , was prepared by adding a dilute solution of ammonia to a concentrated solution of mercuric chloride. When heated, a third of the nitrogen is evolved in the free state and the remainder as ammonia. The solid residue consists of mercurous chloride mixed with a relatively small quantity of ammonium chloride.

The action of ammonia on mercurous chloride was examined. When ammonia is passed over dry mercurous chloride, scarcely any action takes place at first, but after some time the additive compound, HgCl, NH_3 , is formed. By the action of aqueous ammonia on mercurous chloride, dimercuroammonium chloride, $\text{NH}_2\text{Hg}_2\text{Cl}$, is produced. Even when the ammonia is dry, however, some ammonium chloride is formed, proving that substitution takes place, and a small quantity of dimercuroammonium chloride is formed.

When "infusible white precipitate" is boiled for a considerable time with water, hydrated dimercuriammonium chloride, $\text{NHg}_2\text{Cl}, \text{H}_2\text{O}$, is formed. When this is heated, almost the whole of the nitrogen is evolved in the elementary condition, and free mercury is also obtained as well as mercurous chloride.

By the action of potassium hydroxide on the double salt,



dimercuriammonium bromide, $2\text{NHg}_2\text{Br}, \text{H}_2\text{O}$, was obtained, which decomposes on heating in precisely the same way as the corresponding chloride. J. McC.

Dimercuriammonium Nitrate. PRAFULLA CHANDRA RÂY (*Zeit. anorg. Chem.*, 1902, 33, 209—211. Compare Trans., 1902, 81, 644).—When a solution of dimercuriammonium nitrite is stirred into concentrated nitric acid by means of a pipette, a white, amorphous powder of dimercuriammonium nitrate, $2\text{NHg}_2\text{NO}_3, \text{H}_2\text{O}$, is obtained.

It decomposes, when heated, without melting and the residue consists essentially of mercuric oxide.

It is identical with "mercuroxyammonium nitrate," obtained by shaking a concentrated solution of mercuric nitrate with dilute ammonia. J. McC.

Separation of the Cerite Elements by means of Chromic Acid. C. RICHARD BÖHM (*Zeit. angew. Chem.*, 1902, 15, 1282—1299).—When a solution of the rare earths in chromic acid is fractionally precipitated with potassium chromate, the earths are separated in the following order: I. Cerite earths: (a) cerium, (b) lanthanum, (c) praseodymium, (d) neodymium, (e) samarium. II. Ytterite earths: (f) terbium, (g) ytterbium, (h) erbium, (i) yttrium, (k) gadolinium. Any of the rare earths may, therefore, be concentrated in a small bulk and its isolation for technical purposes be much facilitated. In order to be successful, the precipitation must take place in very dilute and boiling solutions, and the precipitates should be very finely divided.

Tables are given showing the colours of the chromates, oxalates, and oxides of the various fractions, their microscopic appearance, and spectroscopic behaviour (also compare Abstr., 1902, ii, 455).

L. DE K.

Catalytic Action of Aluminium Chloride in the Reactions of Sulphuryl Chloride (Dissociation Catalysis). OTTO RUFF (*Ber.*, 1902, 35, 4453—4470. Compare Abstr., 1901, ii, 500; 1902, ii, 13).—By the direct action of liquid sulphur dioxide on aluminium chloride in a sealed tube, a well-defined, crystalline compound, $\text{AlCl}_3\cdot\text{SO}_2$, is obtained. It is produced also by the action of aluminium chloride on sulphuryl chloride according to the equation: $\text{AlCl}_3 + \text{SO}_2\text{Cl}_2 = \text{AlCl}_3\cdot\text{SO}_2 + \text{Cl}_2$, for it can be shown that whilst a current of dry carbon dioxide passed through a flask containing sulphuryl chloride carries sulphur dioxide and chlorine with it in equivalent proportions, there is an excess of chlorine evolved when aluminium chloride has been added to the sulphuryl chloride; further, if the temperature is gradually raised to 120° , the residue in the flask is largely $\text{AlCl}_3\cdot\text{SO}_2$. These preliminary experiments led to the view that the reaction expressed by the above equation is reversible, and accordingly the author has studied the effect of varying the concentrations of the reacting substances. It is not possible, however, to obtain a satisfactory equilibrium constant, and this is traced to another reaction, namely: $\text{AlCl}_3\cdot\text{SO}_2 \rightleftharpoons \text{AlCl}_3 + \text{SO}_2$. The compound $\text{AlCl}_3\cdot\text{SO}_2$ is stable at 100° in an atmosphere of sulphur dioxide, but in sulphuryl chloride solution it can be entirely decomposed at the ordinary temperature by carrying off the free sulphur dioxide with a current of dry carbon dioxide. The net result, therefore, of adding aluminium chloride to sulphuryl chloride is the simultaneous production of sulphur dioxide, chlorine, and the double compound $\text{AlCl}_3\cdot\text{SO}_2$, in other words, aluminium chloride increases the extent to which sulphuryl chloride is dissociated.

The experiments recorded above explain the catalytic effect of aluminium chloride on a reaction previously studied (*loc. cit.*):

$2S + SO_2Cl_2 = S_2Cl_2 + SO_2$; for in this paper it has been shown that chlorine is liberated in the interaction of aluminium chloride and sulphuryl chloride, and free chlorine converts sulphur into disulphur dichloride even at the ordinary temperature.

The effect of aluminium chloride is therefore not a purely catalytic one, inasmuch as the catalyser is itself involved in the equilibrium. The case is somewhat akin to those of "pseudo-catalysis" (Wagner, *Abstr.*, 1899, ii, 275; although Ostwald proposes the term "Uebertragungskatalyse"). The author suggests that the name "dissociation catalysis" be applied to those cases where the effect of the catalyser is to increase the dissociation of one of the reacting substances.

J. C. P.

Aluminium Fluoride. E. BAUD (*Compt. rend.*, 1902, 135, 1103—1106).—When alcohol is added to a neutral solution of alumina in hydrofluoric acid, a crystalline precipitate of $Al_2F_6 \cdot 7H_2O$ is formed, which is easily soluble in water. Its heat of solution at 15° is 3 Cal. The heats of solution of this salt and of the insoluble aluminium fluoride hydrate of the same composition in hydrofluoric acid differ by 1 Cal., which corresponds with the heat change in the transformation of the soluble into the insoluble modification. In a current of hydrogen at 110 — 120° , $4H_2O$ are expelled; at 150 — 170° , H_2O is driven off, and at 210 — 250° a sixth H_2O is liberated, and the residue is $Al_2F_6 \cdot H_2O$. At a red heat, anhydrous aluminium fluoride volatilises, but with much decomposition.

The monohydrate is insoluble in water, and its heat of solution in hydrofluoric acid at 15° is 51.55 Cal., whilst that of the insoluble heptahydrate is 8.88 Cal. The difference, 42.27 Cal., corresponds with the fixation of $6H_2O$. From the analogy with the heat of hydration of aluminium chloride, the heat of formation of the solid monohydrate from solid aluminium fluoride and liquid water is deduced to be 23.68 Cal., and consequently:

Al_2F_6 (solid) + $7H_2O$ (liquid) =

$Al_2F_6 \cdot 7H_2O$ (solid) $\left\{ \begin{array}{l} \text{insoluble.....} + 65.95 \text{ Cal.} \\ \text{soluble} + 64.95 \text{ Cal.} \end{array} \right.$

The heat of formation of anhydrous aluminium fluoride from the elements is found to be 499 Cal., which is the greatest of all the aluminium and halogen compounds.

J. McC.

The Acid Reaction of Alums and the Influence of this Acidity in the Action of Chrome Alum on Gelatin. AUGUSTE LUMIÈRE and ALPHONSE SEYEWITZ (*Bull. Soc. chim.*, 1902, 27, [iii], 1073—1077).—The quantity of sulphuric acid liberated, as measured by the amount of sodium hydroxide necessary to produce a slight permanent precipitate, when chrome alum is dissolved in water at from 0° to 50° is 8.435 per cent., and in water at 100° 12.8 per cent.; the amount of acid liberated by dissolving iron or aluminium alum is, at any temperature, 5.134 per cent. These values are those required by a progressive decomposition of the kind $2(M_2O_3, 3SO_3) \rightarrow 2M_2O_3, 5SO_3 + SO_3 \rightarrow 2M_2O_3, 4SO_3 + 2SO_3$; this decomposition being

complete in the case of chrome alum, but arrested at the end of the first stage with the other alums.

The rate of solidification of gelatin solutions by chrome alum solutions increases with the concentration of the former, but decreases with that of the latter, the acidity neutralising the hardening effect of the chromium salt. The product is not insoluble in boiling water unless the amount of gelatin in the final solution is at least 10 per cent., and that of chrome alum at most 2.5 per cent. When chrome alum solutions are first neutralised with sodium hydroxide, their effect on gelatin solutions increases with the mass added, up to a certain limit, beyond which further addition produces no effect.

T. A. H. •

The Violet Manganic Metaphosphate described by Gmelin. PHILIPPE BARBIER (*Compt. rend.*, 1902, 135, 1054—1055).—The violet manganic metaphosphate described by Gmelin is obtained by heating precipitated manganese dioxide with 4.5 times its weight of phosphoric acid solution of sp. gr. 1.70 until nearly dry, then adding 2 more parts of phosphoric acid, and heating until the mass acquires a peach-blossom colour. It has the composition $\text{Mn}_2(\text{PO}_3)_6$, is insoluble in water, but dissolves in hydrochloric acid with liberation of chlorine, and is decomposed by alkali hydroxides with separation of manganic oxide.

C. H. B.

A Violet Ammonio-manganic Phosphate. PHILIPPE BARBIER (*Compt. rend.*, 1902, 135, 1109—1110).—By heating a mixture of precipitated manganese dioxide and diammonium hydrogen phosphate made up to a paste with water, a decomposition takes place with liberation of ammonia. The product is heated with syrupy phosphoric acid until it becomes violet. On washing out with water, an insoluble, violet powder of the composition $\text{Mn}_2\text{P}_4\text{O}_{14} \cdot 2\text{NH}_3$ is left. This ammonio-manganic dipyrophosphate is decomposed by hydrochloric acid and by alkalis. When heated to redness, it leaves a residue of manganous metaphosphate.

J. McC.

Manganese Aluminate. ÉMILE DUFAU (*Compt. rend.*, 1902, 135, 963—964).—A mixture of 100 parts of alumina and 230 parts of manganous oxide is heated in the electric furnace for three minutes by a current of 1000 amperes at 60 volts. The product is boiled with hydrochloric acid, then freed from graphite by throwing the powder into methylene iodide. The *manganese aluminate* has the formula MnAl_2O_4 ; it is obtained in clear, yellow, octahedral crystals of about the same hardness as quartz, and has a sp. gr. of 4.12 at 20°. It is quite stable at the ordinary temperature, but when heated in air darkens owing to a superficial oxidation. Sulphur has no action on it at the melting point of glass. It is attacked when heated in fluorine, but bromine and iodine have no action on it. It is insoluble in hydrochloric acid, but is readily attacked by hydrofluoric, nitric, or sulphuric acid, and is easily disintegrated by fusion with alkali chlorate, nitrate, oxide, or carbonate.

J. McC.

Theory of Oxidation Processes. WILHELM MANCHOT (*Annalen*, 1902, 325, 93—104. Compare Abstr., 1900, ii, 546; 1901, ii, 549).—In many processes of oxidation, oxygen is rendered active and

capable of effecting certain oxidations which ordinary oxygen will not perform. According to the author, an addition of whole molecules of oxygen to the substance oxidised first occurs; the fate of these "primary oxides," which generally possess a peroxide character, is varied (Engler and Wöhler, *Abstr.*, 1902, ii, 127). Rarely they are the final products of oxidation, although this case seems to have been observed not unfrequently in the formation of organic peroxides. More generally, the "primary oxide" decomposes into the final product of the oxidation and "active oxygen," which occasionally appears as oxygen gas, but more frequently combines with some oxidisable substance in the system; this oxidisable substance is called the "acceptor" (compare Engler and Wöhler, *loc. cit.*), and may either be a further portion of the substance which forms the primary oxide, or it may be some third substance. Stress is laid on the fact that the primary oxide is the first step in oxidation, and that the final product is only formed from this primary oxide; thus, in the oxidation of ferrous to ferric salts, the primary oxide, which contains quadrivalent or quinquivalent iron according to the oxidising agent used, is the first product of oxidation; it breaks down into the ferric salt and "active oxygen," which then oxidises a further portion of the ferrous salt to ferric salt, the ferrous compound in this case being the "acceptor."

The apparent reduction by means of hydrogen peroxide is due to the formation of a highly oxidised primary product, which then breaks down. In this case, the final substance is less oxidised than the original material, the hydrogen peroxide.

It is thought that although there is little hope of isolating these primary oxides, yet their existence must be granted, just as in organic chemistry the necessity of supposing a primary additive process has lately become recognised.

K. J. P. O.

Formation of Peroxide in the case of Iron. WILHELM MANCHOT [with O. WILHELMS] (*Annalen*, 1902, 325, 105—124. Compare preceding abstract).—A large number of experiments have been made on the oxidation of ferrous salts by means of oxygen, chromic acid, permanganic acid, hydrogen peroxide, and hypochlorous acid. In order to determine the nature of the "primary oxide" in each case, the oxidation was carried out in the presence of an "acceptor," by which the "primary oxide" was reduced to ferric salt. When the oxidation was effected by chromic acid, hydriodic acid, which was not oxidised under the conditions, was used as "acceptor"; a dilute solution of ferrous salt was run into a solution containing chromic acid and hydriodic acid and the iodine set free during the process titrated by thiosulphate. It was found that each equivalent of iron required three equivalents of oxygen; the "primary oxide" is therefore Fe_2O_5 . In the absence of the "acceptor," hydriodic acid, the primary oxide would break down into ferric salt and oxygen, which would be utilised in oxidising a further quantity of ferrous salt, acting as "acceptor."

Permanganic acid similarly appears to produce the "primary oxide"

Fe_2O_5 ; in this case, as the result of numerous experiments, it was found that tartaric acid was the most convenient "acceptor." The ferrous salt was added to a solution containing permanganic, tartaric, and sulphuric acids, and the excess of permanganic acid estimated by titrating the iodine set free from hydriodic acid. Hydrogen peroxide (Abstr., 1901, ii, 658) produces the "primary oxide" Fe_2O_5 . Oxygen gas, on the other hand, seems to lead only to the production of FeO_2 as "primary oxide." Experiments with hypochlorous acid, which did not give very certain results, indicate that for each equivalent of iron four equivalents of oxygen are required; the "acceptor" in this case was tartaric acid.

Persulphuric, chloric, bromic, iodic, and nitric acids all behave in a similar manner, but means of carrying out quantitative experiments could not be devised.

According to the views here expressed, not only should ferrous salts be oxidised to "primary oxides," which then oxidise the "acceptors," but ferric salts should also be able to effect the oxidation of the "acceptors." Experiments have shown that ferric salts can act in this manner, but ferric salts act more slowly than do ferrous salts, or, in other words, ferrous salts yield the "primary oxide" more readily than ferric salts. Comparative experiments have been made on the decolorisation of indigo in the presence of ferrous or ferric salts by nitric acid, potassium persulphate, chlorate, bromate, and iodate, and sodium hypochlorite, to demonstrate this fact.

Contrary to Ostwald's opinion that acids hasten oxidation processes (Abstr., 1888, 1024), it is found that the oxidising action of hydrogen peroxide is hindered.

The "primary oxides," the existence of which is assumed in these processes, have in no case been isolated.

K. J. P. O.

Peroxidation of Chromous Compounds. WILHELM MANCHOT and O. WILHELMS (*Annalen*, 1902, 325, 125—128. Compare preceding abstracts and Abstr., 1901, ii, 549).—The oxidation of chromous oxide by the oxygen of the air has been investigated. The chromous oxide was used in the form of chromous oxalate, which is easily prepared and is stable. The chromous oxalate was dissolved in a concentrated alkaline solution of potassium arsenite, which acted as "acceptor"; the solution was placed in a nitrometer, filled with moist oxygen, and the absorption of oxygen measured. In the presence of the acceptor, two equivalents of oxygen were absorbed for each equivalent of chromous oxide. When oxidised by oxygen, the "primary oxide" is CrO_2 .

K. J. P. O.

Colloidal Hydroxides. WILHELM BILTZ (*Ber.*, 1902, 35, 4431—4438).—The use of metallic nitrate solutions is recommended for the preparation of colloidal hydroxides, since it has been previously shown that the nitrate ion has not so great a precipitating action as most other anions. Kuhne's parchment tubes were employed, but it was not found possible to obtain the dialysed colloidal solution free from nitrate.

Colloidal chromic hydroxide solution is perfectly clear, has a dark

green colour, and is quite neutral. Ferric hydroxide solution has a brownish-red colour and is not affected by boiling. The solution of stannic hydroxide is cloudy, and when warmed readily coagulates. With aluminium nitrate, the greater part of the salt dialyses through the parchment, and only a very dilute colloidal solution of the hydroxide is obtained.

Colloidal solutions of cerium hydroxide, thorium hydroxide, and zirconium hydroxide have been prepared. The cerium hydroxide solution, when evaporated, leaves a dry, gummy mass free from ammonium salts, but containing nitrate. Zirconium hydroxide solution has a faintly acid reaction.

The coagulating influence of $N/5$ solution of different electrolytes on the various colloidal solutions has been studied. The thorium hydroxide solution appears to be the most stable, and the chromic hydroxide solution relatively stable. The cerium hydroxide solution is very readily coagulated.

The "gold number" (compare Zsigmondy, *Abstr.*, 1902, ii, 188) for zirconium hydroxide solutions varies from 0.046 to 0.09.

J. J. S.

Observations on Uranous Oxide. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1902, 135, 900—901).—Whilst uranyl chloride, when calcined in the air, is converted into the oxide, U_3O_8 , uranyl bromide readily gives up the whole of its bromine, leaving the oxide, UO_2 , as a brick-red mass which is very stable at high temperatures; when heated in a current of hydrogen, it changes into a black modification, without, however, losing an appreciable amount of oxygen. It is suggested that this decomposition may be utilised for determining the mol. weight of uranous oxide and also for checking the atomic weight of bromine.

K. J. P. O.

Antimony Pentaiodide. R. W. EMERSON MACIVOR (*Chem. News*, 1902, 86, 223—224).—In earlier experiments with mixtures of iodine and antimony (this *Journal*, 1876, i, 329), as in more recent ones in which Pendleton's directions (*Abstr.*, 1884, 19) were followed, the author has failed to obtain antimony pentaiodide; he doubts its existence, and regards Pendleton's product as a mixture of iodine and the triiodide.

D. A. L.

Action of Tellurium and Selenium on Gold and Silver Salts. ROY D. HALL and VICTOR LENHER (*J. Amer. Chem. Soc.*, 1902, 24, 918—927. Compare *Abstr.*, 1902, ii, 402).—Tellurium easily reduces gold chloride solution; the precipitation is complete, but the tellurium must be finely powdered or it becomes coated with gold and further action is prevented. Tellurium reduces silver solutions with formation of silver telluride, which in turn is able to reduce solutions of gold salts. The silver telluride formed in this way behaves quite similarly to that prepared from silver tellurite, and to the native substance.

Selenium is not such an active reducing agent. It only reduces gold solutions when boiled. On reduction of silver solutions, silver

selenide is formed, which acts as a reducing agent towards gold chloride solution.

In addition to the minerals previously examined (*loc. cit.*), it has been found that calaverite, hessite, and krennerite reduce gold chloride solutions to metallic gold.

J. McC.

Monochloroplatinic Acid. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1902, [v], 11, ii, 241—248; 271—275).—The author's researches were made with a view to determining the constitution of the compound first obtained by Herschel in 1832 (*Ann. Pharm.*, 3, 337) by the action of sunlight on chloroplatinic acid in presence of lime, and subsequently examined by several other chemists. His results confirm the view of Miolati (*Zeit. anorg. Chem.*, 1900, 22, 464; *Abstr.*, 1900, ii, 214), that the compound is a calcium salt having the composition $[\text{PtCl}(\text{OH})_5]\text{Ca}, \text{H}_2\text{O}$. The corresponding barium and strontium salts were also prepared by a similar method and analysed. If alkali hydroxides are employed in place of the alkaline earths, similar salts are not obtained, but non-chlorinated products result, so that other metallic derivatives of the acid, $[\text{PtCl}(\text{OH})_5]\text{H}_2$, must be prepared from the alkaline earth salts. The *silver*, *basic lead*, $[\text{PtCl}(\text{OH})_5]\text{Pb}, \text{Pb}(\text{OH})_2$, *thallium*, and mercury salts were thus prepared and analysed.

Monochloroplatinic acid, $[\text{PtCl}(\text{OH})_5]\text{H}_2$, prepared by the action of dilute sulphuric acid on the barium salt, was obtained as a brown, deliquescent syrup; it is dibasic and its solutions decompose carbonates slowly in the cold, but readily on heating.

T. H. P.

Mineralogical Chemistry.

Analysis of Combustible Gas evolved in the Caspian Sea near the Gulf of Baku. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 712—713).—Two samples of combustible gas obtained from different parts of the Caspian Sea gave the following results on analysis: (1) methane, 96.28, and nitrogen, 3.72 per cent.; (2) methane, 95.17, and nitrogen, 4.83 per cent.

T. H. P.

Presence of Argon, Carbon Monoxide, and Hydrocarbons in the Gases of the Fumerolles of Mount Pelée in Martinique. HENRI MOISSAN (*Compt. rend.*, 1902, 135, 1085—1088).—The samples of gas analysed were collected from a fumerolle between the eruptions of May 8th, 1902, and August 30th, 1902. The temperature of the gases at the exit was about 400°. The gas was saturated with water and contained traces of hydrogen chloride and sulphur vapour. No hydrogen sulphide, acetylene, ethylene, or helium could be detected.

The following percentages were found: carbon dioxide, 15·38; oxygen, 13·67; nitrogen, 54·94; argon, 0·71; carbon monoxide, 1·60; methane, 5·46; hydrogen, 8·12.

The relative proportion of argon to nitrogen and oxygen is remarkably high, and shows that it does not come from an admixture of the gas with air during the collection. The quantity of carbon monoxide present is sufficient to produce a toxic effect.

J. McC.

Composition of Fire-damp from the Coal-mines of the Donetz. NICOLAI S. KURNAKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 654—659).—The author gives analyses of samples of fire-damp collected in the coal-mines of the Donetz basin. The following are typical results, and refer to gases taken at different depths; the numbers give percentages by volume:

	CO ₂ .	CH ₄ .	O.	N.
1	1·04	64·91	3·60	30·45
2	0·29	51·96	8·09	39·66
3	0·57	61·08	3·81	34·50

T. H. P.

Nickel contained in Nickelpyrrhotite from Sudbury in Canada. C. W. DIXON (*Chem. Centr.*, 1902, ii, 1148; from *Eng. and Min. J.*, 1902).—When the non-magnetic portions are removed as completely as possible from very pure nickelpyrrhotite, the percentage of nickel is reduced from 4—5 to 0·68—1·20. Hence only a small portion of the nickel is contained in the pyrrhotite, the remainder being present in another mineral, which analysis has shown to be pentlandite, (NiFe)S.

E. W. W.

Calcite-sand Crystals. EDWIN H. BARBOUR and CASSIUS A. FISHER (*Amer. J. Sci.*, 1902, [iv], 14, 451—454).—Calcareous sandstones, composed of indistinct crystals having the form of calcite but enclosing about 64 per cent. of sand, are distributed over a wide area in South Dakota, Nebraska, and Wyoming. The habit of the crystals differs from that of the well-known "Fontainebleau limestone." Analyses by W. Warner of: I, a sand-crystal, and II, a sand-concretion, gave:

SiO ₂ .	Fe ₂ O ₃ + Al ₂ O ₃ .	CaCO ₃ .	MgCO ₃ .	P.	Undetermined (Mn?).
49·32	14·21	33·27	3·14	0·011	0·049
47·94	14·52	34·24	3·25	0·010	0·040

L. J. S.

Melanochalcite, Keweenawite, &c. GEORGE A. KOENIG (*Amer. J. Sci.*, 1902, [iv], 14, 404—416).—Melanochalcite, a new mineral. Amongst the copper-ores of Calumet, near Bisbee, Arizona, are hard, spheroidal nodules occurring embedded in a brownish-red, clayey matrix. These consist of a nucleus of cuprite surrounded by a zone, a few millimetres in thickness, of a pitchy-black mineral, and outside this of banded zones of malachite, chrysocolla, and quartz. The black

mineral is lustrous and banded in structure, or dull and without banding: it is extremely brittle; $H = 4$. The fine powder is coffee-brown, and under the microscope is translucent, yellowish-brown, and isotropic: sp. gr. = 4.141. The mineral is readily decomposed by hydrochloric acid, leaving a white skeleton of silica. The three following analyses prove it to be a basic silico-carbonate of copper with the formula $\text{Cu}_2(\text{Si,C})\text{O}_4, \text{Cu}(\text{OH})_2$:

CuO.	SiO ₂ .	H ₂ O.	CO ₂ .	Fe ₂ O ₃ .	ZnO.	Total.
76.72	9.91	12.52		0.19	—	99.34.
76.46	8.83	14.20		0.14	—	99.63.
76.88	7.80	7.71	7.17	0.07	0.41	100.04.

Keweenawite, a new mineral.—This occurs with domeykite and mohawkite in a vein in amygdaloidal rock in the Mohawk mine, Keweenaw Co., Michigan. It is massive, very finely granular, and of a pale pinkish-brown colour with metallic lustre; on exposure, it tarnishes to brownish-red; sp. gr. 7.681. The three following analyses agree approximately with the formula $(\text{Cu,Ni,Co})_2\text{As}$:

As.	Cu.	Ni.	Co.	Fe.	Quartz.	Total.	(Cu,Ni,Co):As.
36.96	39.12	17.96	0.94	trace	4.98	99.96	1.915:1
34.18	53.96	9.74	0.94	—	0.78	99.60	2.276:1
[38.42]	40.72	19.42	0.82	trace	0.60	100.00	1.926:1

Mohawkite, domeykite, &c. (Compare Abstr., 1901, ii, 108, 515).—Analyses are given of several other samples of copper arsenide from the Mohawk mine; these vary considerably in appearance and composition (the ratio of Cu:As reaching as high as 30:1), even in the same specimen, and they are rather of the nature of alloys than definite mineral species.

L. J. S.

Borates from Argentina. H. BUTTGENBACH (*Zeit. Kryst. Min.*, 1902, 37, 175; from *Ann. Soc. geol. Belg.*, 1901, 28, Mem. 99—116).—A description is given of several mineral borates from the "Salinas grandes" on the Argentine border of Bolivia and Chile. Analyses of very impure ulexite agree approximately, after deducting impurities, with the usual formula. Pandermite, when examined in thin sections under the microscope, was found to have optical characters identical with those of colemanite. The following analyses of pandermite from Sultan Tchair, Asia Minor, also point to the identity of this mineral with colemanite:

B ₂ O ₃ .	CaO.	H ₂ O.	Total.
50.12	29.94	19.94	100.00
50.26	31.42	18.32	100.00

L. J. S.

Two Rare Minerals found on the Caucasus in the Batoum Province. G. P. TSCHERNIK (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 684—695).—The two minerals were found in granite masses in Batoum,

The first, a variety of samarskite, is velvety, black and crystalline, having a conchoidal fracture and giving a reddish-brown streak; sp. gr. 5.485, hardness 5.5. Analysis gave:

Ta ₂ O ₅ .	Nb ₂ O ₅ .	Y ₂ O ₃ .	Er ₂ O ₃ .	Ce ₂ O ₃ .	La ₂ O ₃ .	Di ₂ O ₃ .	ThO ₂ .
26.88	33.80	6.65	2.72	3.82	1.07	0.74	4.23
ZrO ₂ .	U ₂ O ₃ .	FeO.	MnO.	CaO.	TiO ₂ .	WO ₃ .	SnO ₂ .
2.17	4.35	7.36	traces	0.94	0.60	1.90	traces
MgO.	K ₂ O and Na ₂ O.	Al ₂ O ₃ .	GlO.	H ₂ O.	Total.		
traces	0.48	0.80	0.25	0.22	99.03		

The following formula is assigned to it: $2[(Ce_2O_3, La_2O_3, Di_2O_3)(Ta_2O_5)_3]$, $5[(Y_2O_3, Er_2O_3)(Nb_2O_5)_3]$, $U_2O_3, 2ZrO_2, ThO_2, mFeO, nCaO, [TiO_2, WO_3, GlO, Al_2O_3, (K_2O, Na_2O), H_2O]$.

The second, a specimen of columbite (niobite), has an iron-black colour and metallic lustre and exhibits irregular fracture and a dark brown streak; hardness 6, sp. gr. 5.396. Analysis gave:

Nb ₂ O ₅ .	Ta ₂ O ₅ .	FeO.	MnO.	WO ₃ .	SnO ₂ .
62.80	19.72	11.16	2.85	0.14	0.60
ZrO ₂ .	SiO ₂ .	Al ₂ O ₃ .	Total.		
0.54	traces	traces	99.01		

which leads to the formula: $m(FeO, Nb_2O_5), m'(FeO, Ta_2O_5), m''MnO, SnO_2, ZrO_2, WO_3$.
T. H. P.

Composition of Dumortierite. W. E. FORD (*Amer. J. Sci.*, 1902, [iv], 14, 426—430).—Previous analyses of dumortierite show considerable variations, and the following were undertaken with a view of establishing a formula for the mineral. Analysis I is of material from Clip, Arizona; II, of lavender-coloured material from San Diego Co., California; III, from Harlem, New York:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	B ₂ O ₃ .	H ₂ O.	Total.	Sp. gr.
I.	29.86	63.56	0.23	5.26	1.41	100.32	3.319
II.	30.58	61.83	0.36	5.93	2.14	100.84	3.226—3.43
III.	31.24	61.26	0.10	6.14	2.09	100.83	3.211—3.302

Regarding the alumina, boron trioxide and water as bases, there may be deduced from these analyses the acid $H_{60}Si_7O_{44}$; if the hydrogen of this acid be wholly replaced by aluminium, the formula becomes $Al_{20}Si_7O_{44}$, or, as a basic orthosilicate, $(AlO)_{16}Al_4(SiO_4)_7$. In analysis I, in which the ratio of $B_2O_3 : SiO_2 = 1 : 7$, the formula approximates very closely to $[AlO]_{16}Al_2B_2(SiO_4)_7$.

Dumortierite, as small spherules of a beautiful blue colour and with radially fibrous structure, occurs embedded in a light coloured, siliceous gangue on the North Fork, Skamania Co., Washington. L. J. S.

Trachyte from Monte Amiata in Tuscany and the Supposed Element X contained therein. G. STURLI (*Gazzetta*, 1902, 32, ii, 208—210).—Trachyte from Monte Amiata, sp. gr. 2·357, gave on analysis :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	TiO ₂ .	CaO.	MgO.	MnO.
61·04	18·84	3·43	1·42	traces	3·32	0·94	—
K ₂ O.	Na ₂ O.	Li ₂ O.	H ₂ SO ₄ .	Cl.	P ₂ O ₅ .	H ₂ O.	Total.
5·91	2·73	0·03	0·13	0·01	—	1·92	99·72

Of the two unknown substances found by Williams (*Neues Jahrb. Min.*, 5, 381) in such trachyte, the first, precipitated by the action of hydrogen sulphide, is shown by the author to be a basic chloride of iron, whilst the second, obtained in heavy, white flocks when the precipitated iron and aluminium hydroxides and silica are fused with potassium hydrogen sulphate and the mass extracted with water, consists of calcium sulphate together with traces of calcium phosphate and silicate.

T. H. P.

The Salt and Water of Kef-el-Melah in the Djebel Amour, OCTAVE LE COMTE (*J. Pharm. Chim.*, 1902, [vi], 16, 475—478).—Analyses of the salt deposits and saline water of this district.

G. D. L.

Physiological Chemistry.

Digestion and Absorption in the Stomach and Small Intestine. E. ZUNZ (*Beitr. chem. Physiol. Path.*, 1902, 3, 339—364. Compare Abstr., 1902, ii, 672).—In dogs, after the ingestion of known amounts of proteid food, the contents of the stomach and first part of the small intestine were examined, and the products separated as in previous work.

Attention is drawn to the comparatively small amount of absorption in the stomach, the relatively small amount of peptone found, the existence of a new group of substances termed "peptoids," which give the biuret reaction and appear to be intermediate between the peptones and their simple decomposition products, which are also found.

W. D. H.

Influence of Oxygen on Proteolysis in Presence of Chloroform. G. MALFITANO (*Ann. Inst. Pasteur*, 1902, 16, 853—856).—In certain cases, proteolysis is stopped by chloroform in absence of oxygen, although in the presence of oxygen the chloroform has no effect or only diminishes the action slightly. This is the case in the autoprotoleolysis of anthrax bacilli and of fibrin and in the proteolytic action of a mixture of pancreatic juice and intestinal juice on white of egg.

The action of pepsin is considerably diminished by chloroform, and the presence or absence of oxygen produces no further modification of the action.

A. H.

Influence of Hydroxyl Ions on Tryptic Digestion. ARISTIDES KANITZ [and ALBERT DIETZE] (*Zeit. physiol. Chem.*, 1902, 37, 75—80).—Dietze (*Inaug. Diss. Leipzig*, 1900) has investigated the digestion of fibrin by pancreatin in the presence of calcium, strontium, and barium hydroxides, and found that all three hydroxides behave in a similar manner and exhibit a maximum effect when present as $N/140$ — $N/300$ solutions.

It would follow, therefore, that the accelerating influence is greatest with solution of hydroxyl ions with a concentration of $N/70$ — $N/150$.

When potassium carbonate solutions are employed, the maximum effect is produced with concentrations of $N/13.8$ — $N/20$. Using Shields's data for the hydrolysis of aqueous solutions of alkali carbonates (*Abstr.*, 1893, ii, 449), these would indicate a concentration of $N/200$ with regard to hydroxyl ions.

J. J. S.

The Glycogen-splitting Ferment of the Liver. FRIEDEL PICK (*Beitr. chem. Physiol. Path.*, 1902, 3, 163—183).—The transformation of glycogen into sugar has been attributed by some to a specific ferment, by others to the "vital" activity of the liver cells. This difference of opinion is now rather a matter of words only, seeing that the existence of intracellular enzymes performing portions of the metabolic work of cell protoplasm is admitted. The extracts were in the present experiments made with a 2 per cent. solution of sodium fluoride dissolved in physiological saline solution. These extracts contain the ferment which converts glycogen into sugar. This power is destroyed by heat. The activity of the ferment was measured by precipitating the unchanged glycogen by means of alcohol and weighing this. The activity of the liver ferment is greater than that of the blood and lymph, but less than that of the kidney. The ferment is therefore believed to exist in the liver cells, and as they die can be more readily extracted from them. Its action is lessened by quinine, and slightly by methyl-violet. The end product is mainly dextrose.

W. D. H.

Utilisation of Glycerol in the Organism and its Estimation in the Urine. H. LEO (*Pflüger's Archiv*, 1902, 93, 269—276).—The method adopted for estimating the glycerol consists briefly in extracting the dried urine with alcohol and ether, getting rid of nitrogenous substances by silver nitrate, and distilling off the glycerol. If small quantities of fat are given to human beings, the urine contains no glycerol; if the dose is increased to 20 grams, traces are found. After a dose of 26 grams, from 0.5 to 1 gram of glycerol is found in the urine; the excretion is completed within six hours. This shows that the greater part of the glycerol of the fat in the food is burnt in the

organism, and that in the metabolism of adipose tissue there is probably no greater liberation of glycerol than can be burnt off.

W. D. H.

Inorganic Metabolism in Horses. FERENCZ TANGL (*Landw. Versuchs-Stat.*, 1902, 57, 367—404).—Experiments are described in which two horses were fed with 8 kilos. of hay, and two with 5 kilos. of hay and 4 kilos. of oats. The total nitrogen, calcium, magnesium, and phosphorus were determined in the food, urine, and faeces. The hay contained very little calcium, a normal amount of magnesium, and a very large amount of phosphorus. In the first experiment, (hay alone) the amount of food was insufficient, and resulted in a loss of weight. In experiment (2), there was an increase in weight.

In experiment (1), the loss of phosphorus in the faeces equalled the amount supplied in food; in experiment (2), it was somewhat less; but the urine contained much more than in experiment (1).

The results relating to nitrogen show a loss when the horses received hay alone, and a gain with hay and oats. There was, however, a slight gain of calcium even when the horses received hay alone; there was also a gain of magnesium in both experiments.

The results show that with ordinary feeding with hay and oats far less calcium is necessary to maintain equilibrium than is indicated by Wolff's results.

N. H. J. M.

Physiological Experiments during Two Balloon Journeys. HERMANN VON SCHROETTER and NATHAN ZUNTZ (*Pflüger's Archiv*, 1902, 92, 479—520).—Ten hours in a balloon at the height of 5000 metres produced no morphological changes in the blood. Pulse and blood-pressure were also apparently unaffected. The reduction power of the tissues, tested by Hénocque's method, showed no change. Pulmonary ventilation was increased; this, however, was not the result of lessened barometric pressure, but of other meteorological factors. The respiratory quotient increases when a height of over 4000 metres is reached, but the height at which this begins varies with the individual. Subjective sensations, due to diminution of oxygen, do not run parallel with the objective expression of these in the change of the respiratory quotient. The small increase of oxygen absorbed noted in some experiments is explained by the increased rate of breathing and the action of other muscles, for example, shivering, fidgeting about, &c.

W. D. H.

The Blood in High Altitudes. EMIL ABDERHALDEN (*Pflüger's Archiv*, 1902, 92, 615—622. Compare Abstr., 1902, ii, 619—672).—Explanatory of former work, and polemical against van Voornveld (*Pflüger's Archiv*, 1902, 92, 1).

W. D. H.

Modifications in the Blood-gases under the Influence of Ethyl Chloride, Croton-chloral, and Chloralose. CH. LIVON (*Compt. rend. Soc. Biol.*, 1902, 54, 1319—1320).—With chloroform, ether, and chloral, the proportion of carbon dioxide in the blood falls,

and the oxygen increases, as several other observers have found. Ethyl chloride produces the same effect. With croton-chloral, the same occurs if anæsthesia is not complete, but when anæsthesia is complete, and the same is true for chloralose, the opposite condition is produced.

W. D. H.

Carbon Monoxide in the Blood of Isolated Animals and of Fishes. MAURICE NICLOUX (*Compt. rend. Soc. Biol.*, 1902, 54, 1167—1169. Compare Abstr., 1901, ii, 518).—Dogs in the country have less carbon monoxide in their blood than those kept in Paris. This seemed to show that atmospheric conditions influence the amount of gas. In the present experiments, the animals were kept on rocky islets in the sea in as pure an atmosphere as possible. Their blood yielded nearly as much of the gas as those living in Paris. This can hardly be accounted for by the small amount of carbon monoxide in the air, and the hypothesis that this gas is a metabolic product is supported by the fact that fishes' blood yields it also.

W. D. H.

Albumoses in the Blood. LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1902, 3, 373—377).—In view of the importance of the question raised by Embden and Knoop as to whether albumoses are found in the blood (this vol., ii, 86), it is necessary to study their origin: whether they are present in normal blood, whether absorbed from the alimentary canal, or formed by ferment action in the blood itself. Zanetti has drawn attention to the presence of a mucoid in ox-blood (*Ann. Chim. Farm.*, 26, 12). The present research on horse serum shows the presence of one or more proteids which are not coagulable by heat, which give albumose reactions, and one of which is allied to the mucoid just mentioned.

W. D. H.

Blood Coagulation in Invertebrates. VIRGILIO DUCCESCHI (*Beitr. chem. Physiol. Path.*, 1902, 3, 378—384).—The blood of the Echinoderm, *Strongylocentrotus*, of the worms *Sipunculus* and *Phymosoma*, and of the common crustaceans was examined. Large amounts of neutral salts hinder coagulation. Soluble oxalates do not prevent the formation of the plasmodium of cells, which is regarded as the basis of the clot, unless added to saturation. The formation of the gelatinous substance, which in crustacea takes place in addition to the fibrin-like substance formed by the processes of the cells, is, however, prevented by small amounts of oxalate. Drugs like cocaine (added to the blood, or injected previously into the animal) or chloroform, if allowed to act long enough, which render the corpuscles immobile (especially those termed explosive cells by Hardy), prevent coagulation.

W. D. H.

Carbon Dioxide as an Agent in Producing Artificial Parthenogenesis in Star-fish. YVES DELAGE (*Compt. rend.*, 1902, 135, 570—573, 605—608. Compare Abstr., 1901, ii, 611).—Previous experiments on artificial parthenogenesis have led to inconclusive results; some eggs undergo no change. But if the sea-water is saturated with carbon dioxide, division always occurs; indeed, this reagent is stated to

be more efficacious than spermatozoa. Its action is not to influence the osmotic relationships, and the terms specific stimulant and catalytic action are dismissed as meaningless. The action is attributed to the poisonous action of the gas, and to the fact that it is readily got rid of.

W. D. H.

Permeability of Leucocytes and Lymph Cells by Anions of Sodium Salts. HARTOG J. HAMBURGER and H. J. VAN DER SCHROEFF (*Chem. Centr.*, 1902, ii, 1057—1058; from *Arch. Anat. Physiol.; physiol. Abth.*, 1902, 119—165. Compare Hamburger and v. Lier, this vol., ii, 87).—The same methods were employed as in previous work on red corpuscles, and corresponding results were obtained. This is regarded as important from the pharmacological standpoint, as it shows that the cells of lymph glands and leucocytes are affected by the sodium salts used as drugs; anti-bacterial action is also to be explained on the permeability of the cells.

W. D. H.

Demarcation Currents Produced by Chemical Reagents. MARTIN HENZE (*Pflüger's Archiv*, 1902, 92, 451—472).—The poisonous action of various substances on frog's muscle was detected by the demarcation current set up. In each case, the strength of the solution and the magnitude of the electrical disturbance are given and plotted out in curves. The substances found to act positively were caffeine, muscarine, choline, veratrine (this alkaloid has other actions also due to stimulation of sarcoplasm), protoveratrine, nicotine, quinine, ammonium chloride, potassium chloride, potassium cyanide, sodium cyanide (this is due to the cyanogen ion). The substances which gave a negative result are strychnine, morphine, cocaine, atropine, antiarine, strophantine, helleboreine, pelletierine, physostigmine, and urethane.

W. D. H.

Influence of Calcium and Potassium Salts on the Tone of Plain Muscle. PERCY G. STILES (*Amer. J. Physiol.*, 1903, 8, 269—272).—Calcium salts used in minimal amount increase the tone of muscle, and this action is antagonised by potassium salts. This is now a matter of common knowledge. It is, however, unsafe to infer that the influence of a salt is always the same without considering the concentrations; for instance, when 0.2 per cent. or more of potassium chloride is present, the action is the exact contrary to that which is usually taught.

W. D. H.

Autolysis in Fish-flesh. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1902, 3, 266—276).—The flesh of fish, like mammalian flesh, undergoes a process of auto-digestion under conditions in which micro-organisms are excluded. A remarkable point about this is that the ferments to which this is due can act in the presence of brine, and it is this process which causes the ripening of pickled herrings and the like. The subject is therefore one of commercial importance. The fat fish ripen most readily. Hydroxy-acids are formed from unsaturated fatty acids. Xanthine bases are also formed in abundance.

W. D. H.

The Ash of New-born Children and of Human Milk. FRIEDRICH SÖLDNER and WILLIAM CAMERER (*Zeit. Biol.*, 1902, 44, 61—77. Compare Abstr., 1902, ii, 413).—Further analyses on this subject are given, which are stated not to support Bunge's views on the question. W. D. H.

Iodine in Bony Tumours with Thyroid-like Structure. EDGAR GIERKE (*Beitr. chem. Physiol. Path.*, 1902, 3, 286—287).—The tumours occurring in bone, which have a structure recalling that of the thyroid are regarded as metastases, which have their origin as a primary and malignant new growth in the thyroid itself. This form of adeno-carcinoma may, however, be latent in the thyroid. Ewald found iodine in similar metastases in lungs and lymphatic glands. Colloid material and, in some cases, iodine in relatively large amount were also obtained in the present research on bony tumours. W. D. H.

Phosphorus in Animal Tissues. A. L. PERCIVAL (*Compt. rend.*, 1902, 135, 1005—1007).—The phosphorus in tissues is divided into (1) inorganic, (2) conjugated [as in lecithin, nuclein, &c. (*sic*)], and (3) organic. The third term is not fully defined. Under these three heads, the amount is tabulated for most of the organs and tissues of the body. General conclusions are hardly attempted, and the original tables must therefore be consulted. W. D. H.

Distribution of Calcium in Animal Organisms. M. TOYONAGA (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 143—154).—Calcium and magnesium were determined in the separated grey and white substances of the brain of a horse and a calf. It was found that the grey substance contained less ash, but much more calcium and magnesium, than the white substance; the former contains more calcium than magnesium, the latter more magnesium than calcium. N. H. J. M.

The Formation of Glycine from Leucine in the Body. RUDOLF KOHN (*Chem. Centr.*, 1902, ii, 1063—1064; from *Arch. exp. Path. Pharm.*, 48, 177—183).—In opposition to Wiener (*Arch. exp. Path. Pharm.*, 40, 313) it is found that benzoic acid is toxic in spite of the simultaneous administration of leucine. Leucine-hippuric acid was not found in the urine, nor does glycine originate directly from the leucine. W. D. H.

Influence of Catalytic Agents on the Functions of the Organism. Spermin, Cerebrin, and Adrenal Hydrochloride. ALEXANDRE DE POEHL (*Compt. rend.*, 1902, 135, 1141—1143).—*Spermin*, $C_5H_{14}N_2$, one of the oxydases, acts as a positive catalyser in the oxidation processes which take place in the body; it therefore neutralises the effect of plasmatic poisons, which diminish the energy of oxidation. *Cerebrin*, a ferment present in the leucomains of the nervous tissue, acts similarly.

Chloradrenal (adrenal hydrochloride), $C_{10}H_{15}O_4N.HCl$, exercises a

catalytic influence on reduction processes, and its effects can be destroyed by spermin.

The action of the spermin is connected with the alkalinity of the blood. In all states of fatigue, there is an accumulation of organic acids which diminishes the alkalinity and the catalytic oxidation of spermin. On the other hand, the alkalinity cannot rise beyond a certain limit on account of the production of carbon dioxide, and the oxidation process is, at any rate partially, regulated by this mechanism.

J. McC.

Animal Tyrosinase. C. GESSARD (*Compt. rend. Soc. Biol.*, 1902, 54, 1304—1306). **Animal Antityrosinase.** C. GESSARD (*ibid.*, 1398—1399; Compare Abstr., 1902, i, 196).—The statements of von Fürth, Schneider, Przibram, &c., are confirmed that the enzyme called tyrosinase plays an important part in the production of melanins; the present experiments relate to the ink of the sepia. Serum prepared with vegetable tyrosinase, and which inhibits its action, has no such action on animal tyrosinase. Serum prepared with animal tyrosinase has no action on vegetable tyrosinase, but it has a slight anti-action on animal tyrosinase. Two rabbits were used in these experiments, and in only one did the serum contain this feeblar antityrosinase.

W. D. H.

The Wine-red Bodies in Holothurians. CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1902, 37, 89—93).—The so-called wine-red bodies in holothurians are in the main the same as the uncoloured "chalky bodies," which consist chiefly of calcium carbonate. They, however, contain iron and phosphorus. Their reddish-brown colour is due, not to an organic pigment but, to iron.

W. D. H.

Ichthylepidin. CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1902, 37, 83—89).—This substance is found in the scales of most teleostean fishes. Green and Tower (Abstr., 1902, ii, 415) have pointed out that to this rule *Mola mola* is an exception. Another exception is *Tinca vulgaris*, where the substance is present in so small a quantity that its detection is difficult.

W. D. H.

The Electrical Conductivity of Urine in Relation to its Chemical Composition. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1902, 24, 996—1004).—The conductivity and sp. gr. of urine were determined, as well as the urea, and the chlorine present as sodium chloride. The conductivity varies with the amount of inorganic salts present, but as the quantity of sodium chloride is large no importance attaches to the conductivity itself. After deducting the fraction of the conductivity due to sodium chloride, the remainder is of importance for indicating the extent of certain metabolic changes. As the conductivity is easily determined, the variations in the value of the residual conductivity may be used to fix the lag in the rate of inorganic excretion.

J. McC.

Physiological Effect of Manganese and Experiments on the Influence of Manganese and Iron on Peptic Digestion. GORTHEILF COHN (*Chem. Centr.*, 1902, ii, 1268—1269; from *Inaug.-Diss.*, Berlin).—The original paper contains a *résumé* of the literature concerned with the toxicological effect of manganese, and a description of experiments which show that the presence of manganese salts, and more particularly of iron salts, interferes with artificial digestion by means of pepsin.
E. W. W.

Behaviour of Carvone and Santanol in the Animal Body. HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1902, 36, 441—451. Compare Abstr., 1901, ii, 180).—Since Harries (Abstr., 1901, i, 551) has shown that carvone, when shaken with air, takes up one atom of oxygen and is converted into a derivative containing a hydroxyl group, it is possible that this substance may suffer a similar oxidation in the animal body; the derivative would then be able to form a "conjugated" glycuronic acid. Although carvone has a distinctly poisonous action on rabbits, evidence was obtained of the presence of a conjugated glycuronic acid in the urine after feeding with carvone, but no definite carvone derivative could be got from this conjugated acid by decomposition with acid.

Santanol, which can easily be given as food, appears as a conjugated glycuronic acid which can be isolated as a lead salt. The potassium salt, $C_{16}H_{24}O_9K_2$ or $C_{16}H_{22}O_9K_2$, is obtained as a very hygroscopic substance, but not in a definitely crystalline state. Treatment of the salt with acids leads to hydrolysis, a compound $C_{10}H_{18}O_3$ being formed; the latter is probably derived from santanol by elimination of the isoprene group, C_5H_6 , and simultaneous oxidation of a methyl group to carboxyl.
K. J. P. O.

Fate of some Cyclic Terpenes and Camphor in the Animal Body. HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1902, 36, 452—461).—Conjugated glycuronic acids can always be isolated as basic lead salts of the form $(R \cdot CO_2)_2Pb, 2PbO, 3H_2O$. At the same time, there is frequently produced a dibasic acid which yields a lead salt, $R(CO_2)_2Pb, 2PbO$. The latter compound is obtained from the ortho-class of terpenes, thujone, limonene, &c., the oxidation not only leading to the formation of a hydroxyl group, but also to the conversion of a methyl group into carboxyl. The camphor group behaves in a similar manner, whereas the *pseudo*-terpenes, sabinene, camphene, &c., give only hydroxyl derivatives. *m*-Methylisopropylbenzene appears as *m*-cymylglycuronic acid, and in this respect behaves differently from the para-derivative, which is oxidised to cuminic acid.
K. J. P. O.

Action of Fluorescent Substances [on Infusoria]. OSKAR RAAB (*Zeit. Biol.*, 1902, 44, 16—27. Compare Abstr., 1900, i, 425).—Solutions of quinoline-red, harmalin, and eosin show towards *Paramæcium* the same action as was previously found with other fluorescent substances. The action of non-fluorescent substances, such as magenta and crystal-violet, is not influenced by light. Other opinions previously expressed on this subject are confirmed by further

experiments. Sunlight will cause local necrosis in the ears of mice if eosin has been injected previously.

W. D. H.

Physiological Action of Pilocarpine. OTTO FRANK and FRITZ VOIT (*Zeit. Biol.*, 1902, 44, 111—120).—It is well known that pilocarpine increases the activity of most secreting glands. In the present research on dogs, particular attention is drawn to the increase of saliva and loss of water by the skin. This is accompanied by an elevation of body temperature and an increased discharge of carbon dioxide. Whether the latter is due to an increased formation of the gas or an increase in the secretory activity (Bohr) of the pulmonary epithelium cannot be decided until analyses are made of the gases of the blood in these circumstances.

W. D. H.

Poisonous Action of Ions, and the Part Played by the Valency of Cathions in this Relation. JACQUES LOEB and WILLIAM J. GIES (*Pflüger's Archiv*, 1902, 93, 246—268).—Further experiments confirming the views previously expressed by Loeb on this subject (*Abstr.*, 1900, ii, 227, 491, 555). Solutions of non-electrolytes (urea, cane-sugar, glycerol, alcohol) have no antitoxic action except where the non-electrolyte, as in the case of sugar, decreases the concentration of the poisonous ions by the formation of compounds which are dissociable with difficulty. The influence of lecithin, which is present in all protoplasm, is important in modifying the antagonistic action of ions, for, as W. Koch has shown, this substance is precipitated by electrolytes with bivalent cathions, but not by those with univalent cathions.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of the Prolonged Action of the Temperature of Liquid Air on Micro-organisms, and the Effect of Mechanical Trituration at the Temperature of Liquid Air on Photogenic Bacteria. ALLAN MACFADYEN (*Proc. Roy. Soc.*, 1902, 71, 76—77).—The author's earlier investigations (*Abstr.*, 1900, ii, 610) have been supplemented by extending the time for which certain micro-organisms were exposed to the temperature of liquid air. The following organisms were thus exposed for six months: *Bacillus typhosus*, *B. coli communis*, *Staphylococcus pyogenes aureus*, and a *Saccharomyces*. In no case could any impairment of the vitality of the organisms be detected.

When photogenic bacteria are subjected to mechanical trituration at the temperature of liquid air (compare *loc. cit.*), their luminosity is abolished.

J. C. P.

Intracellular Toxin of the Typhoid Bacillus. ALLAN MACFADYEN and SYDNEY ROWLAND (*Proc. Roy. Soc.*, 1902, **71**, 77—78).—Disintegration of typhoid bacilli at the temperature of liquid air has shown that they contain an intracellular toxin. J. C. P.

Chemical Products of *Bacillus coli communis* and *Bacillus lactis aerogenes*. LEO F. RETTGER (*Amer. J. Physiol.*, 1903, **8**, 284—293).—Both bacilli fail to cause much decomposition in peptone bouillon, but they rapidly decompose an egg-meat mixture. Among the products of the colon bacillus are indole, scatole, phenols, aromatic hydroxy-acids, scatolecarboxylic acid, hydrogen sulphide, mercaptan, tyrosine, leucine, and tryptophan. Proteoses and peptone are present in only small amounts, probably being broken up rapidly into simpler substances. Diamines are absent. This bacillus is much more rapid in its action than the other. Finally, such simple substances as carbon dioxide, water, and methane are formed. This takes many weeks; it is at present doubtful how far such results may be applied to what takes place in the alimentary canal, where the time at the disposal of the bacteria is much shorter. The conditions in the intestine are, however, favourable to rapid decomposition. W. D. H.

Nitrogen Assimilation and Proteid Formation of Moulds. FRIEDRICH CZAPEK (*Beitr. chem. Physiol. Path.*, 1902, **3**, 47—66. Compare this vol., ii, 35).—The present paper deals with the utilisation of nitrates, organic nitro-derivatives, hydrazines, oximes, aromatic cyclic compounds, cyanides, and thiocyanates.

Aspergillus niger assimilates the nitrogen of inorganic nitrates, ammonium nitrate giving better results than the potassium salt. Nitromethane was utilised, but there was not very much growth. Methylhydrazine gave good results, whilst phenylhydrazine is useless. Acetaldoxime and acetoxime were not utilised. The aminophenols and 2:4-diaminophenol gave good results. *o*-Aminobenzaldehyde gave unsatisfactory results, whilst with *o*-aminoacetophenone there was no growth at all. *m*-Aminobenzoic acid, in conjunction with sugar, was found to be suitable, whilst the para- and especially the ortho-derivatives were much less so. Sodium thiocyanate gave moderately good results; potassium ferrocyanide gave no growth at all, and potassium ferricyanide and sodium nitroferricyanide very little.

As regards sources of carbon, the hexoses are the best, but even methylal considerably increased the growth of *Aspergillus* when given with asparagine, as compared with asparagine alone. Ethylene glycol is very unsuitable, and propylene glycol useless; *l*-xylose is equal in value to dextrose. Dulcitol produced very little growth as compared with the other substances, less even than methylal. N. H. J. M.

Occurrence of Glycogen in Distillery Yeasts, Press Yeasts, and Top Brewery Yeasts. WILHELM HENNEBERG (*Chem. Centr.*, 1902, ii, 1515—1516; from *Woch. Brau.*, 19, 651—652).—The quantity of glycogen depends on the character of the culture medium. When cultivated in 1 per cent. aqueous solutions of sugar, the cells contain

only a small quantity, but in 10—20 per cent. solutions a very large quantity of glycogen is formed. Maltose, grape-sugar, and dextrose behave similarly in this respect, but solutions of starch and dextrin, even with addition of peptone and solutions of peptone or asparagine alone, do not permit of the formation of glycogen. Glycogen is formed more slowly in sugar peptone solutions and disappears more quickly. Potato mash never contains a large quantity, but corn- or maize-mash, molasses, and malt seasonings are generally rich in glycogen. Lactic acid mashes, in which more than 1 per cent. of acid is present, contain less than sweet mashes.

The formation of glycogen depends also on the kind of yeast and its sensitiveness to alcohol. The behaviour of glycogen in dead cells was also investigated. The presence of glycogen is an indication of the presence of considerable quantities of sugar, but probably confers no special advantage on the yeast and cannot, therefore, be regarded as a "reserve material."

E. W. W.

Decomposition of Proteids by means of Bacteria. ALONZO ENGLEBERT TAYLOR (*Zeit. physiol. Chem.*, 1902, 36, 487—492).—In order to ascertain whether bacteria decompose proteids into the same substances as do acids or unorganised ferments (zymases), a large quantity of casein was submitted to the action of pure cultures of *Bacillus coli communis* and *Proteus vulgaris* for several weeks. The micro-organism first mentioned gave rise only to albumoses; the latter produced together with indole and scatole small quantities of diamino-acids, probably lysine and histidine.

K. J. P. O.

The Influence of Bacteria on the Decomposition of Bone. JULIUS STOKLASA [with F. DUCHÁČEK and J. PITRA] (*Beitr. chem. Physiol. Path.*, 1902, 3, 322—338).—Powdered bone suspended in a suitable solution was subjected in flasks to the action of thirteen kinds of bacteria; these are divided into two groups: (1) the common bacteria which produce putrefaction, including some which are pathogenic; (2) denitrification bacteria. The nitrogen in solution was examined by Hausmann's method; in the case of the first group, it was principally in the form of amino-nitrogen; in the second group, the diamino-nitrogen was most abundant. The amount of phosphoric acid which goes into solution as the result of the action of the denitrification bacteria is smaller than is the case when members of the first group are employed. If sugar is added to the nutrient solution, among other products alcohol is found. Some of the bacteria are spoken of as ammonia-producing. A further communication on the proteolytic enzyme of the bacteria is promised.

W. D. H.

Decomposition of Fodder and Foods by Micro-organisms.
III. Organisms producing "Ropiness" and Slime in Milk.
 JOSEF KÖNIG, ALB. SPIECKERMANN, and J. TILLMANS (*Zeit. Nahr. Genussm.*, 1902, 5, 945—961. Compare Abstr., 1901, ii, 676, and 1902, ii, 686—687).—The bacteria which cause "ropiness" in milk belong to various species. Some apparently are of the type *Bacterium lactis acidii* Leichmann, others convert milk sugar into volatile and non-

volatile acids as well as into gaseous substances, whilst others, again, have no acid-forming action on milk sugar. Some, as *Bacterium lactis aërogenes*, decompose butter fat, and casein is destroyed by *Bacterium K*. In all the experiments carried out by the authors, a loss of total solids in the milk was noticed. Acetic acid was produced by all the bacteria as a decomposition product, and formic acid was detected in the case of *Bacillus Guillebeau* and *Bacterium K*. With regard to the non-volatile acids, *Bacterium lactis aërogenes* formed succinic acid, *Bacterium K*. and *Bacillus bruxellensis* also producing this acid as well as traces of lactic acid.

W. P. S.

Physical Conditions of Tuberisation. NOEL BERNARD (*Compt. rend.*, 1902, 135, 706—708).—The results of experiments with potatoes in solutions of dextrose and potassium chloride showed that the production of tubers depends on the degree of concentration of the solution. The degree of concentration in the sap suitable for the production of tubers may, under normal conditions, be attained by the intervention of parasites. Other conditions, particularly those affecting transpiration, also perhaps come into action.

N. H. J. M.

Variation of the Carbohydrate Reserves in the Stems and Roots of Woody Plants. LECLERC DU SABLON (*Compt. rend.*, 1902, 135, 866—868).—Experiments with different trees (chestnut, quince, pear, and peach) showed that the sum of the carbohydrates convertible into dextrose is lowest in May and highest in October and November. Both the stems and roots act as organs of reserve. Generally the roots contain more than the stems, especially in autumn and winter; the roots contain more sugar than the stems during active growth.

N. H. J. M.

Galactose, a Product of the Action of Seminase on Vegetable "Albumen." HENRI HÉRISSEY (*Compt. rend. Soc. Biol.*, 1902, 54, 1174—1176).—Among the products of digestion produced by the action of seminase on the mannans and galactans of the albuminous corms of leguminous plants, mannose has already been separated. The present paper gives an account of experiments which resulted in obtaining galactose also in a crystalline form.

W. D. H.

Production of Alcohol in Phænogams. T. TAKAHASHI (*Bull. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 243—246. Compare Godlewski and Polzeniusz, *Abstr.*, 1901, ii, 618).—Sterilised peas (33·3795 grams) kept in water for 38 days, produced much carbon dioxide and nearly 1 gram of ethyl alcohol. A number of the peas retained their germinating power. The water in which the peas had been kept was found to contain 4·01 per cent. of the original dry matter.

Experiments in which separated kernels or skins of peas were kept in 10 per cent. dextrose showed that zymase was absent. The production of alcohol was therefore due to the protoplasm itself.

N. H. J. M.

Formation of Chlorophyll [in Seedlings] in Rarefied Air and Rarefied Oxygen. JEAN FRIEDEL (*Compt. rend.*, 1902, 135, 1063—1064).—Seedlings germinated in the dark and then exposed to light in air at about one-fifth the normal pressure, remain etiolated and show practically no formation of chlorophyll. If, however, they are placed in oxygen at the same pressure, the production of chlorophyll takes place with practically the same rapidity as under normal conditions. The relative pressure of the oxygen surrounding the plants has great influence on the formation of chlorophyll, but the total pressure has no recognisable effect. Experiments were also made with seedlings in atmospheres containing at least the normal amount of carbon dioxide, but an insufficient quantity of oxygen; in these conditions very little chlorophyll was formed. C. H. B.

Acids of the Fat of the California Bay Tree. JOHN M. STILLMAN and E. C. O'NEILL (*Amer. Chem. J.*, 1902, 28, 327).—From the seeds of the *Umbellularia Californica*, the authors had previously obtained a substance which they regarded as a homogeneous acid, $C_{11}H_{22}O_2$ (Abstr., 1882, 1185); this has now been found to be a mixture of acids, of which lauric acid is one. A. McK.

Oil from Water-Melon Seeds. MISS S. WOJNAROWSKAJA and MISS S. NAUMOVA (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 695—697).—On extracting water-melon seeds with light petroleum, they yield 21·4 per cent. of a slow drying oil, which solidifies at -20° and has the sp. gr. 0·925 at 15° . The following constants have been determined: Hehner number, 96·1; Köttstorfer number, 198; Reichert number, 0·4; Hübl number, 111·5; free acid, 0·4; acetyl number, 4·7; Maumené's test, $50·4^{\circ}$; Livache's test, 2·7 per cent. The constants for similar oils are given for comparison. T. H. P.

Active Principle contained in the Seeds of *Dregea rubicunda*. W. KARSTEN (*Chem. Centr.*, 1902, ii, 1514; from *Ber. Deutsch. Pharm. Ges.*, 12, 245—250).—From the seeds of *Dregea rubicunda* collected by Busse in Ugogo about 2·5 per cent. of a glucoside which does not appear to be identical with strophanthin has been isolated by Thoms' method (Abstr., 1898, i, 328). The glucoside, which probably has the composition $C_{19}H_{30}O_{10}$ or $C_{23}H_{38}O_{12}$, is an amorphous, slightly greenish-yellow powder, has at first a burning, bitter taste which soon becomes nauseous, is hygroscopic but not deliquescent, and on exposure to air gradually turns lemon-yellow. It melts at 85° , or after dehydration over sulphuric acid at 107° , is readily soluble in water, alcohol, benzene, chloroform, or glacial acetic acid, and does not reduce Fehling's solution even on warming. The glucoside is completely decomposed by a 2 per cent. solution of sulphuric acid at 60° , and has a physiological action similar to that of strophanthin; the latter is, however, about five times as poisonous as the former.

The seeds do not contain alkaloids or trigonelline. A small quantity of a base was isolated from the fruit skins but no glucoside was detected.

E. W. W.

Occurrence of Strophanthin, Choline, and Trigonelline in *Strophanthus hispidus*. W. KARSTEN (*Chem. Centr.*, 1902, ii, 1514; from *Ber. Deutsch. Pharm. Ges.*, 12, 241—245).—The fresh roots of *Strophanthus hispidus* from Togo were found to contain, not only 0.6—0.7 per cent. of strophanthin, but also 1 per cent. of trigonelline, and a certain amount of choline. These substances were isolated by Thoms' method (*Abstr.*, 1898, i, 328). The properties of the strophanthin thus obtained and of the strophanthidin prepared from it were identical with those of the compounds described by Thoms (*loc. cit.*; compare also Feist, *Abstr.*, 1898, i, 329), but the carbohydrate obtained by the decomposition of strophanthin by dilute hydrochloric acid is probably rhamnose; it crystallises in plates and melts at 106°.

E. W. W.

Vegetation of Odoriferous Plants. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Ann. Agron.*, 1902, 28, 595—616. Compare *Abstr.*, 1901, ii, 67; 1902, ii, 99, 246, and 523).—The plant selected for investigation was *Mentha piperita*. The composition of the essence varies according to conditions of climate, cultivation, &c., but the following substances are always present: *l*-pinene, cadinene, eucalyptol and menthol, acetaldehyde and valeraldehyde, menthone, a lactone $C_{10}H_{16}O_2$, and acetic and valeric acids; menthyl acetate and valerate are also present.

Addition of sodium chloride and nitrate to the soil increases the percentage amount of organic matter in the plant and is also favourable to etherification. Sodium chloride hinders the formation of menthone, whilst sodium nitrate is favourable to the essence.

N. H. J. M.

Chemical Investigations on Cocoa-Nuts and Remarks on the Changes during Germination. J. E. KIRKWOOD and WILLIAM J. GIES (*Chem. Centr.*, 1902, ii, 1365; from *Bull. Torrey Bot. Club*, 29, 321—352. Compare *Abstr.*, 1901, ii, 267).—The endosperm of cocoa-nuts contains: oil, 37.29; crude fibre, 3.39; and nitrogen, 0.74 per cent. The proteids of the endosperm consist almost exclusively of globulin and albumoses, only traces of albumin and nuclein being present. The globulin, as separated, always contains some polysaccharide, which has to be removed by means of diastase. The purified substance contains 18.2 per cent. of nitrogen and has the properties of edestin.

N. H. J. M.

Cocoa-Seed Shells (Preparation of Theobromine. Xanthine Derivatives. Method of Detection of the Shells). J. DEKKER (*Chem. Centr.*, 1902, ii, 1217—1218; from *Schweiz. Woch. Pharm.*, 40, 436—439, 441—444, 451—454).—A sample of commercial cocoa-seed shells was found to contain 0.9 per cent. of cotyledon residues. The unroasted shells contained 3.6 per cent. of fat, 5.7 ash, 2.24 nitrogen, 0.19 theobromine-nitrogen, 2.05 proteid-nitrogen = 12.8 albumin, whilst the roasted shells contained 3.8—4.0 fat, 7.8—8.1 ash, 1.82 nitrogen, 1.63 proteid-nitrogen = 10.2 albumin. Theobromine dissolves in 1800 parts of water at 15°, in 3570 of absolute alcohol, 3845 of chloroform,

25,000 of ether, 3845 of ethyl acetate, 100,000 of benzene, 1250 of amyl alcohol, 50,000 of a 10 per cent. solution of fat in light petroleum, 137 of a 10 per cent. solution of ammonia, and in 132 of an 18 per cent. solution of ammonia. It is insoluble in light petroleum, but dissolves in 100 parts of boiling chloroform, and is decomposed by lime-water. 0.58 per cent. of theobromine may be obtained from the shells by treating with magnesia, boiling with water, evaporating the filtrate, and boiling the residue with chloroform. A small quantity of caffeine is also present, but adenine and theophylline could not be detected.

Adulteration of cocoa powder by the addition of seed shells may be detected by estimating the percentage of pentosans; cocoa kernels contain 2.17—2.41 per cent., the shells 8.18—9.63, and pure Dutch cocoa 2.56. The pentosans cannot be extracted from the shells by water. Methylpentosan was found in the shells but not in the kernels.

E. W. W.

Composition of the Skins of Olives and a New Compound contained in them. EDOARDO PEANO (*Chem. Centr.*, 1902, ii, 1365; from *Staz. sperim. agrar. ital.*, 35, 660—664).—In the original paper, the composition of olive-skins is given. In order to extract the fat, carbon disulphide is used and not ether, as the latter also dissolves a substance contained in the epicarp of the fruit. The latter compound may be isolated by extracting the fat and then treating with methyl alcohol; it forms a white powder, is not of a waxy nature, melts at 250°, is a weak acid, and is soluble in alcohol, ether, or acetone, but insoluble in water, light petroleum, chloroform, or carbon disulphide.

E. W. W.

Action of Uranium on Plants. OSCAR LOEW (*Bul. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 173—175).—Dilute solutions (0.01 per cent.) of uranium nitrate increased the yields of peas and oats, stimulating the production both of straw and seed. Solutions containing as much as 0.2 per cent. of the salt poisoned young pea plants in three days.

N. H. J. M.

Action of Sodium Fluoride on Plant Life. KEIJIRŌ ASŌ (*Bul. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 187—195).—Solutions containing 0.05 per cent. of sodium fluoride were found to have a more or less injurious effect on the germinating power of seeds. Further experiments with shoots of barley, wheat, and rice showed that, in the case of barley and rice, growth was stimulated by solutions containing 0.001 per cent. of sodium fluoride; wheat was injured by solutions of this quantity of sodium fluoride.

Peas grown in soil (2—3 kilos.) were stimulated by small amounts (0.001 gram) of sodium fluoride.

N. H. J. M.

Action of Highly Diluted Potassium Iodide on Plants. S. SUZUKI (*Bul. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 199—201. Compare Dirks, *Jahresb. Agrik.-chem.*, 1868, 289; Boureçet, *Compt. rend.*, 1899, 129; and Voelcker, *Abstr.*, 1901, ii, 269).—Potassium iodide (0.006 gram in 2—3 kilos. of soil) increased the growth of peas both as regards straw and seed.

N. H. J. M.

Poisonous Action of Potassium Ferrocyanide on Plants. S. SUZUKI (*Bul. Coll. Agric. Tokyo Imp. Univ.*, 1902, 5, 203—205).—Potassium ferrocyanide, in solutions containing as little as 0.001 per thousand, gradually destroyed barley plants. N. H. J. M.

The Amount of Hydrogen Cyanide in Cigar Smoke. JOSEF HABERMANN (*Zeit. physiol. Chem.*, 1902, 37, 1—17. Compare Abstr., 1901, ii, 680).—The smoke obtained when different sorts of cigars are subjected to intermittent burning has been tested, both qualitatively and quantitatively, for hydrogen cyanide. In practically all cases, the acid was present, but the amounts varied considerably. In each experiment, some six to ten cigars were burnt and the products passed through four absorption vessels containing alcoholic potash. In the quantitative experiments, this solution was distilled in steam, when all the hydrogen cyanide was found in the distillate; the acid was removed from the distillate by five or six extractions with ether, and finally absorbed in a 5 per cent. aqueous potash solution by shaking the ethereal solution three to four times with 10—20 c.c. of the alkali. The cyanide was ultimately converted into Prussian blue and weighed as such, special precautions being taken in the weighing.

No cyanide could be detected in the cigar ash. The amounts of acid formed from different brands of cigar do not correspond in the least with the amounts of nicotine present; the hydrogen cyanide is therefore probably derived from proteid substances.

It is shown that neither the free acid nor cyanide are present in the cigars before burning.

The numbers obtained per 100 grams of burnt cigar are: maximum 0.0174, minimum 0.0038, mean 0.0098 gram of hydrogen cyanide. These numbers are considerably lower than those obtained by Vogel (*Ding. Journ.*, 1858, 148, 231) and Kissling (*ibid.*, 1882, 244, 240).

J. J. S.

Potassium Manuring of Barley and Replacement of Potassium by Sodium. P. DOLL (*Landw. Versuchs-Stat.*, 1902, 57, 471—476).—Potassium and sodium chlorides give better results than the sulphates, owing, probably, to the greater diffusibility of potassium chloride and to the potassium of the soil being rendered soluble by the sodium chloride. The results obtained with sodium were only slightly less satisfactory than those obtained with potassium; the best results were obtained when both were employed simultaneously.

The experiments were made in pots, a very sandy soil being employed. N. H. J. M.

Manurial Experiments on Rye with different Forms of Nitrogen. H. CLAUSEN (*Bied. Centr.*, 1902, 31, 799—801; from *J. Landw.*, 49, 365, and *Ill. landw. Zeit.*, 1902, No. 14).—Ammonium sulphate increased the yield of oats (both grain and straw) much more than sodium nitrate. Both manures lengthen the lower portion of the

stems, sodium nitrate having much greater effect than ammonium sulphate. The crop manured with ammonium sulphate is therefore less liable to be laid, notwithstanding the greater yield.

Comparing the results obtained in two seasons, it would seem that sodium nitrate gives better results than ammonium sulphate in dry seasons, whilst in wet seasons ammonium sulphate is preferable.

N. H. J. M.

Poppy and Poppy-seed Cake. F. MACH (*Landw. Versuchs-Stat.*, 1902, 57, 419—459).—Three samples of poppy-seed (1, East Indian, 2, Levant, and 3, Turkish), freed from impurities, were found to have the following percentage composition :

	Water.	Crude pro- teid.	Pro- teid.	Indi- gestible pro- teid.	Amines and amides, &c.	Crude fat.	Crude fibre.	Pent- osans.	N-Free extract.	Pure ash.
1.	4.50	22.68	21.60	2.58	1.08	48.02	5.18	3.44	9.81	6.00
2.	4.28	20.28	18.42	2.39	1.86	50.65	5.38	3.05	10.58	5.56
3.	3.87	20.35	18.88	2.06	1.47	51.40	5.64	3.20	9.50	5.59

The seeds also contain oxalic acid (1.62 per cent. in the Indian seeds) and lecithin (0.91 per cent. in Indian seeds). The ash constituents (per cent. in pure ash) were as follows :

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ + Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .
1.	10.85	0.7	34.9	9.05	2.65	32.1	3.75	1.35
2.	12.25	0.8	33.8	8.65	1.8	33.65	3.75	1.7
3.	11.8	0.9	32.0	8.85	1.9	35.05	3.6	1.05

The physical and chemical constants obtained with the oil showed very little variation in the different seeds.

Analyses were made of four samples of poppy-seed cake. It was shown that Indian cake is free from opium or contains only traces too slight to be injurious.

N. H. J. M.

Potatoes. EMILE BRÉAL (*Ann. Agron.*, 1902, 28, 545—576).—When potatoes are kept through the winter, carbon dioxide and ammonia are liberated. Chloroform vapour checks the liberation of carbon dioxide, and when the action is prolonged the tuber dies and a nitrogenous liquid is produced. Exposure to cold retards the respiration of the tubers and causes the accumulation of a reducing sugar.

The organic nitrogen of potatoes is present partly in an insoluble form, and partly as albumin which coagulates at 70°, and partly as solanine. The tubers contain both nitric acid and ammonia; the nitric acid disappears when an ammonium salt is introduced. Potatoes produce shoots spontaneously in the spring, but require water to form roots. The green substance of the shoots rapidly absorbs starch, and the roots of the shoots absorb ammonia, nitrates, and humic acid. The separated shoots can be made to grow when supplied with suitable mineral food and potassium humate. Roots living in water absorb ammonium salts, but only in absence of nitrates.

N. H. J. M.

Chemical-Geological Investigations on Absorption by Decomposed Rocks. MAX DITTRICH (*Bied. Centr.*, 1902, 31, 793—796; from *Mitt. G. Bad. Geol. Landes-Aufnahme*, 4).—Analyses of weathered hornblende granite showed that considerable amounts of sodium, calcium, and magnesium had been withdrawn, and that a deposition of potassium had taken place. The potassium was nearly all insoluble in water and dilute acids.

In order to ascertain the effect of solutions of salts, the granite (25 grams) was subjected to the action of chlorides and sulphates of alkalis and alkaline earths (100 c.c.) for two days at the ordinary temperature. Sodium chloride (*N/10*) dissolved a good deal of calcium and magnesium, a corresponding amount of sodium being absorbed by the granite; only traces of potassium dissolved. Potassium chloride (*N/10*) dissolved about the same amount of magnesium and about twice as much calcium as sodium chloride; a considerable amount of potassium was withdrawn from the solution. The potassium taken up by the granite was not completely dissolved by dilute acetic acid. Ammonium chloride gave similar results, the ammonia being retained by the granite. Calcium and magnesium chlorides had very little effect. Potassium carbonate dissolved neither calcium nor magnesium, but more than a third of the potassium and a corresponding amount of carbon dioxide were absorbed.

The absorption of potassium is probably due to the presence of calcium and magnesium aluminates. Kaolin does not absorb potassium, as frequently supposed. N. H. J. M.

Vegetation Experiments with Marsh Soil. BRUNO TACKE (*Bied. Centr.*, 1902, 31, 801—804; from *Mitt. Deut. Landw.-Ges.*, 1902, St. 18, 19).—The experiments were made in zinc boxes holding 17 kilos. of soil. Two soils were employed, the one containing 38, the other 26.6, per cent. of clay, the rest being in both cases mostly fine sand. The dry soils contained: K_2O , 0.64 and 0.59; CaO , 0.85 and 0.57; MgO , 1.17 and 1.02; Fe_2O_3 , 13.74 and 11.73; P_2O_5 , 0.15 and 0.60; SO_3 , 0.09 and 0.07; N, 0.26 and 0.30 per cent. respectively. Applications of lime and nitrogen increased the yield of grass. Potassium had very little effect, whilst phosphoric acid had a considerable effect on the first soil, but not on the second.

Further experiments are described which were made to ascertain the effect of drying (by exposure to air) on the solubility of the phosphoric acid and potash. It was found that drying increased the solubility in dilute solvents, the increase being greater when 1 per cent. citric acid was employed than with 1 per cent. hydrochloric acid.

N. H. J. M.

Have Phosphatic and Potassium Manures a Direct Action on Cultivated Plants? CORRADO LUMIA (*Chem. Centr.*, 1902, ii, 1338—1339; from *Staz. sper. agrar. ital.*, 35, 525—549).—From the results of experiments described in the original paper, the conclusion is drawn that mineral manures (potassium, calcium, magnesium, and phosphorus, &c.) act directly on the soil microbes, but only indirectly on plants, their chief rôle being to promote the growth and

activity of nitrifying bacteria and of microbes which assimilate free nitrogen.
N. H. J. M.

Manurial Experiments with Damara and Peruvian Guano. E. SCHREIBER (*Bied. Centr.*, 1902, 31, 798—799; from *Recherches sur la valeur agricole du Damara guano et du Phospho-guano de Pérou*).—The manurial constituents of Damara guano were found to be as follows:

Nitrogen.		P_2O_5 .		K_2O .
Total.	as NH_3 .	Total.	Soluble.	
7.0	5.0	15.0	6.5	3.2

The results of pot experiments with oats showed that the manure is very suitable both for light and heavy soils. Peruvian guano gave good results when applied to light soil, but not with loam.

N. H. J. M.

Experiments on the Treatment of Farmyard Manure with Lime. OTTO REITMAIR (*Chem. Centr.*, 1902, ii, 1339; from *Zeit. Landw.-Versuchswes. Oesterr.*, 5, 1107—1140).—Application of calcium carbonate to farmyard manure was without material effect, and the conclusion is drawn that calcium carbonate is not to be recommended as a preservative when the dung is mixed with straw (without special addition of liquid manure) and contains about 75 per cent. of water.

N. H. J. M.

Analytical Chemistry.

Spectroscopic Detection of Small Quantities of Chlorine, Bromine, and Iodine. JOVAN P. PANAOVIC (*Chem. Centr.*, 1902, ii, 1342; from *Bul. Soc. Sci.*, 11, 390—432).—Lecoq de Boisbaudran's barium process is recommended for the spectroscopical detection of bromine and chlorine. When all three halogens are present, Mitscherlich's process gives satisfactory results. The solution is precipitated with silver nitrate; if the chlorine largely predominates, a small quantity of silver will suffice. The precipitate is dried and mixed with twice its weight of copper oxide, and heated in a current of hydrogen. The hydrogen flame will show in succession the spectra of the copper chloride, copper bromide, and copper iodide.

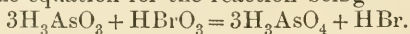
L. DE K.

Simple Qualitative Test for Bromides and Iodides, and a Test for Hydrogen Carbonates. F. MOLLWO PERKIN (*J. Soc. Chem. Ind.*, 1902, 21, 1375—1376).—About 2 c.c. of chloroform are added to the solution to be tested, and then, drop by drop, a solution of calcium or sodium hypochlorite. If iodine is present, it is liberated and

imparts its characteristic colour to the chloroform. On adding excess of hypochlorite, the solution becomes colourless. A few drops of acetic acid are then added, when bromine is liberated from any bromides present.

Carbon dioxide and hydrogen carbonates liberate hypochlorous acid from solutions of hypochlorites. On adding a solution of the substance to be tested to a mixed solution of potassium bromide and bleaching powder, bromine is at once liberated should the substance be a hydrogen carbonate, and may be dissolved by shaking with 2 c.c. of chloroform. Normal carbonates have no action. W. P. S.

Estimation of Bromic Acid by the Direct Action of Arsenious Acid. FRANK A. GOOCH and J. C. BLAKE (*Amer. J. Sci.*, 1902, [iv], 14, 285—292).—Bromic acid is quantitatively reduced by arsenious acid, the equation for the reaction being



In testing the accuracy of the method, definite amounts of arsenious oxide dissolved in potassium hydrogen carbonate were mixed with measured quantities of potassium bromate solution, and acidified with sulphuric acid. After being kept either at the ordinary temperature, on the steam-bath, or at the boiling temperature, potassium hydrogen carbonate was added and the residual arsenious oxide titrated with iodine solution. The conditions of acidity, excess of arsenious oxide, dilution, time of action, and temperature were varied within wide limits without affecting the accuracy of the results. Further experiments were made on the reduction of bromate solutions by acidified potassium iodide, the liberated iodine being titrated with standardised sodium thiosulphate solution. It was found that the reaction required at least 30 minutes for completion, the amount of potassium iodide used being four times the calculated requirement. Variation of other conditions had no effect. All the samples of potassium bromate employed were found to contain small quantities of chlorate.

W. P. S.

Detection of Fluorine in Wine. FRANCESCO TUSINI (*Chem. Centr.*, 1902, ii, 1390; from *Staz. sperim. agrar. ital.*, 35, 654—659).—100 c.c. of wine are rendered alkaline with ammonia, excess of calcium chloride is added, and the whole is heated nearly to boiling. When cold, the precipitate is collected, washed with water, and then transferred to an Erlenmeyer flask by means of a very little water. A little sulphuric acid is now added, the liquid is heated nearly to boiling, and the vapours are tested with test paper prepared as follows: 200 grams of Pernambuco wood are soaked for ten days in 300 c.c. of cold water, and strips of paper are soaked in the solution and carefully dried; they should be preserved in the dark. If the paper turns yellow when exposed to the vapours, hydrofluoric acid is present. L. DE K.

Hartleb's Method for the Estimation of Sulphates in Drinking Water. GIACOMO ROSSI (*Chem. Centr.*, 1902, ii, 1272; from *Staz. sperim. agrar. ital.*, 35, 578—580).—This method (Abstr., 1901, ii, 627)

was only found to give trustworthy results when the quantities of sulphuric acid dealt with were extremely small. W. P. S.

Estimation of Sulphurous Acid by means of Standard Iodine Solution. ARMAND BERG (*Bull. Soc. chim.*, 1902, 27, (iii), 1077—1083).—The low results obtained when solutions containing more than 0.04 per cent. of sulphurous acid are titrated with iodine are shown to be due to oxidation occurring during the titration (compare Volhard, *Abstr.*, 1888, 192). This source of error is avoided by titrating in a three-necked bottle; two of the necks carry burettes containing, respectively, the liquid to be titrated and the standard iodine solution; the third neck is fitted with two glass tubes arranged for the passage of carbon dioxide or recently boiled water as required. The air in the bottle is first displaced by carbon dioxide, and a certain volume of the sulphurous acid solution allowed to flow in; to this, iodine solution in slight excess is added, and any traces of sulphur dioxide washed out of the tubes by a current of boiled water; the titration is then repeated in the opposite order, and in both cases the excess of iodine is determined with thiosulphate solution. More accurate results are secured by enclosing a determinate quantity of the sulphurous acid solution in a tube closed at one end by caoutchouc tubing and a spring clip, and drawn out at the other to a fragile point; the latter is broken, the air of the flask having been previously replaced by carbon dioxide, and a current of the same gas is employed to project the contents of the tube into a slight excess of iodine solution. T. A. H.

A New Form of Kjeldahl Apparatus. VOGTHERR (*Zeit. öffentl. Chem.*, 1902, 8, 444—446).—The boiling with sulphuric acid is carried out in a flask which is closed by a hollow glass stopper, a tube from the top of the latter dipping into a solution of sodium hydroxide contained in a second flask, a bulb on the tube being provided to prevent the sodium hydroxide sucking back into the acid flask. When decomposition is completed, the sodium hydroxide is replaced by standard acid solution, and the distillation of the ammonia proceeded with, after rendering the contents of the decomposition flask alkaline. W. P. S.

Apparatus for the Estimation of Nitrogen. CH. PORCHER and M. BRISAC (*Bull. Soc. chim.*, 1902, 27, iii, 1128—1130).—The apparatus consists of two parts; in one, the decomposition of ammonium salts by sodium hypobromite takes place, the evolved nitrogen being measured in the other part, which is a simple nitrometer. The ammonium salt is placed in a flask closed by a glass stopper through which pass two tubes. One of these tubes widens out just above the stopper into a cylindrical bulb, the latter being provided with a tap-funnel at its upper end. A tap is also placed on the tube between the flask and the bulb. The second tube passes through the bulb, and, on leaving the latter, is connected by an indiarubber tube to the nitrometer. The bulb is partly filled, by means of the funnel, with a solution of sodium hypobromite, and, after adjusting the level of

the nitrometer and the temperature of the flask and bulb by placing them in a cylinder containing cold water, the hypobromite is allowed to run into the flask. Equilibrium of pressure in the bulb and flask is attained by a small opening in the delivery tube just above the surface of the solution in the bulb. The apparatus is also useful for estimating carbon dioxide in carbonates.

W. P. S.

Estimation of Ammonia in Urine. PHILIP SHAFFER (*Amer. J. Physiol.*, 1903, 8, 330—334).—The Schloesing method is untrustworthy. Most other methods are too difficult for clinical work, although some will give correct results. Folin's second method gives accurate results; this consists in driving a current of air through the urine (to which sodium carbonate and sodium chloride have been added) into decinormal acid. Another method described in this paper is a modification of Boussingault's vacuum distillation method, and this also is trustworthy.

W. D. H.

Estimation of the Nitroso-group. ROBERT CLAUSER and G. SCHWEITZER (*Ber.*, 1902, 35, 4280—4284. Compare Abstr., 1901, ii, 422).—The limitations of the method of estimating the nitroso-group, previously described (*loc. cit.*), have been investigated. It has been found that those nitroso-derivatives which can be represented by the expression $\text{CR}_1\cdot\text{C}(\text{NO})\cdot\text{CR}_2$ readily evolve their nitrogen and can be estimated; thus in the case of diphenylnitrosoamine, which possibly is represented by the formula $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NOH}$, the nitroso-group can be estimated. The same holds for nitrosoantipyrine, where a similar linking exists.

An improved type of apparatus is described.

K. J. P. O.

Estimation of Phosphoric Acid by means of Ammonium Phosphomolybdate. GREGORY PAUL BAXTER (*Amer. Chem. J.*, 1902, 28, 298—315).—The conditions most favourable for accurate analysis are as follows: The phosphate solution, containing about 0.1 gram of phosphoric anhydride in 50 c.c. is poured, with vigorous stirring, into a quantity of the usual molybdic acid solution at least 50 c.c. in excess of the amount theoretically necessary to completely precipitate the phosphoric acid. After remaining 16 hours, the precipitate is washed with a 10 per cent. solution of ammonium nitrate, transferred to a Gooch crucible and heated at 300° for at least 2 hours. The precipitate has the formula $(\text{NH}_4)_3\text{PO}_4\cdot 12\text{MoO}_3$. It occludes ammonium molybdate at the moment of precipitation, and later absorbs more of this salt. This occluded ammonium molybdate loses its ammonia at 290° , so that the excess in weight of the precipitate is due to molybdenum trioxide. Under definite conditions the occlusion has a constant value. An excess of 50 c.c. to 70 c.c. of molybdic acid solution gives a precipitate containing 3.742 per cent. of phosphoric anhydride; with an excess of 160 c.c. the percentage is 3.728. The addition of ammonium nitrate hastens the precipitation.

W. P. S.

New Method of estimating Phosphoric Acid and Magnesia with Molybdate. E. RIEGLER (*Zeit. anal. Chem.*, 1902, 41, 675—686).—The yellow ammonium phosphomolybdate precipitate is washed with ammonium nitrate to remove all excess of molybdic acid, then dissolved in ammonia, and the solution precipitated with a small excess of barium chloride. The precipitate, which after drying at 100° contains all the phosphoric acid and molybdic acid present, and has the formula $\text{Ba}_{27}(\text{MoO}_4)_{24}\text{P}_2\text{O}_8 \cdot 24\text{H}_2\text{O}$, is washed and weighed. The amount of the barium precipitate may also be ascertained gasometrically by employing a known quantity of barium chloride, and estimating the excess of barium by converting it into iodate by the addition of iodic acid, and applying the hydrazine method (Abstr., 1902, ii, 696). A simple apparatus for this operation is described and figured.

To employ the method for the estimation of magnesium, the ordinary magnesium ammonium phosphate is prepared, washed, dissolved in nitric acid, and treated as above. Since 1 part of magnesia yields 101 parts of the barium compound, the method is especially suited for the estimation of very small amounts of magnesium. M. J. S.

Detection of Minute Amounts of Arsenic. F. GARRIGOU (*Compt. rend.*, 1902, 135, 1113—1115).—See this vol., ii, 140.

Estimation of Boric Acid occurring naturally in Vegetable Juices. A. HEBEBRAND (*Zeit. Nahr. Genussm.*, 1902, 5, 1044—1049).—Twenty-five to 30 grams of the juice are evaporated with 5 c.c. of 10 per cent. calcium acetate solution and ignited. After removing any iron salts from the hydrochloric acid solution of the ash by precipitation with sodium hydroxide, the boric acid is estimated by the method previously described by the author (Abstr., 1902, ii, 354). Cherry juice was found to contain 4 mg. of boric acid per litre, gooseberry juice 10 mg., orange juice 4 mg., and lemon juice 6 mg.

W. P. S.

Estimation of Potassium by the Modified Finkener Method. HUGO NEUBAUER (*Landw. Versuchs-Stat.*, 1902, 57, 461—470).—A reply to the criticisms of the Association of Agricultural Experiment Stations at the meeting in Hamburg, Sept. 1901 (compare *ibid.*, 57, 11). N. H. J. M.

Simple Method for the Estimation of Potassium in Urine. WILHELM AUTENRIETH and RENÉ BERNHEIM (*Zeit. physiol. Chem.*, 1902, 37, 29—39).—A solution of sodium cobaltinitrite is prepared by dissolving 30 grams of crystallised cobalt nitrate in 60 c.c. of water, adding 50 c.c. of a concentrated sodium nitrite (= 50 grams NaNO_2) solution and 10 c.c. of glacial acetic acid. The solution is left overnight, and then filtered if necessary.

Fifty c.c. of filtered urine is well shaken with 6—10 c.c. of the sodium cobaltinitrite solution and left overnight. The "cobalt yellow" precipitate $[\text{Co}(\text{NO}_2)_6(\text{Na}_x\text{K}_y)_3\text{H}_2\text{O}]$ (compare De Koninck, *Zeit. anal. Chem.*, 1881, 20, 390; Curtman, Abstr., 1882, 95; Bülmann,

Abstr., 1900, ii, 624) is filtered, washed, dried at $110-120^{\circ}$, dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue is moistened with water, and then treated with 10 c.c. of an 18 per cent. solution of perchloric acid, again evaporated to dryness, and extracted with 10 c.c. of 96 per cent. alcohol containing 0.2 per cent. of perchloric acid. The insoluble potassium perchlorate is filtered in a Gooch crucible, washed with alcohol and ether, dried at $120-130^{\circ}$, and weighed. The small amounts of ammonium salts present in urine do not vitiate the final result. J. J. S.

Apparent Loss of Potassium Salts by Ignition. RUDOLF Woy (*Zeit. öffentl. Chem.*, 1902, 8, 389—397).—Titration of the potassium carbonate formed by the complete ignition of known quantities of potassium tartrate gave results considerably below those required by theory. In some cases the apparent loss amounted to as much as 20 per cent., whilst the actual weight of the ash showed an increase. These results were found to be due to the conversion of part of the potassium carbonate into sulphate by the gases from the burner finding their way into the platinum basin. Traces of nitrate were also detected in the ash. On igniting over a spirit flame, or by protecting the basin by an asbestos plate, correct results were obtained. W. P. S.

Preservation of Standard Solutions of Sodium Sulphide. EUGÈNE PROTHIÈRE and ANNA REVAUD (*J. Pharm. Chim.*, 1902, [vi], 16, 484—490).—Solutions of sodium sulphide may be preserved with unimpaired titre if protected from the air by a layer of oil, preferably olive. They are not acted on by light. G. D. L.

Estimation of Calcium and Magnesium in Urine. L. DE JAGER (*Chem. Centr.*, 1902, ii, 1158—1159); from *Centr. med. Wiss.*, 40, 641—644).—The method is briefly as follows:

On titrating urine with $N/10$ sodium hydroxide in the presence of phenolphthalein, the liquid turns red the moment that the acid sodium phosphate has changed into disodium hydrogen phosphate, and all the calcium and magnesium are precipitated as triphosphates. On adding calcium chloride and continuing the titration, the liquid will again turn red the moment all the excess of phosphoric acid is eliminated as calcium triphosphate.

Another portion may now be titrated after removing calcium with sodium oxalate. By allowing for the amount of phosphoric acid present, the calcium and magnesium may be calculated. For further particulars, the original article should be consulted. L. DE K.

Volumetric Estimation of Zinc. FRIEDRICH KÜSTER and FRITZ ABEGG (*Chem. Zeit.*, 1902, 26, 1129).—An outline of a new process shortly to be published in detail. The zinc is isolated as zinc chloride, which is dried at 110° in a current of dry hydrogen chloride. The chlorine is then estimated volumetrically as usual. L. DE K.

Electrolytic Detection and Estimation of Lead. G. MEILLÈRE (*J. Pharm. Chim.*, 1902, [vi], 16, 465—469).—The addition of pure copper sulphate in the toxicological detection and estimation of lead facilitates the destruction of organic matter, and secures complete precipitation of the lead as sulphide. Lead dioxide is then deposited electrolytically from the solution of mixed sulphides in nitric acid.

G. D. L.

Estimation of Lead in Ores. IRVING C. BULL (*Zeit. anal. Chem.*, 1902, 41, 653—674).—A critical comparison of ten recognised methods of estimating lead in its ores, namely, the dry assay, as described by Ricketts and Miller (*Notes on Assaying*), gravimetric estimation as sulphate, as chromate, and as dioxide precipitated electrolytically, and volumetric estimation by Alexander's ammonium molybdate method, Koenig's acidimetric method, Low's oxalate and permanganate method, Sutton's dichromate method with ferrous salt and thiosulphate respectively, and a modification of Low's ferrocyanide method, employing each method on six ores of different chemical composition and widely varying richness; and also investigating the influence of the presence of antimony, bismuth, barium, strontium, and calcium on the volumetric processes. The dry assay and the oxalate method gave seriously discordant results, the remaining methods agreed closely. The volumetric methods were injuriously affected by the impurities added, the dichromate method the most extensively, the ferrocyanide method very slightly, and that only by bismuth and barium.

M. J. S.

Iodometry of Thallium as Chromate. ERWIN RUPP [with ZIMMER] (*Zeit. anorg. Chem.*, 1902, 33, 156—160).—It has been proved that, in neutral solution, thallium chromate is sufficiently insoluble to allow a method for the estimation of thallium to be based on its precipitation in this form. The method recommended is to add a little precipitated calcium carbonate to a known volume of standard potassium chromate solution (5 per cent.) in a 100 c.c. flask, and then run in the solution containing the dissolved thallium salt. The liquid is made up to the mark and filtered, and the excess of chromate determined by adding an acid solution of potassium iodide, and titrating the liberated iodine with standard sodium thiosulphate solution.

J. McC.

Detection of Mercury in Cheese and Flesh from Animals which have been inoculated against Rinderpest. GIUSEPPE OTTELLI (*Chem. Centr.*, 1902, ii, 1275; from *Boll. Chim. Farm.*, 41, 597—600).—Mercury could not be detected in the flesh of animals which had undergone Baccelli's treatment—inoculation with mercuric chloride solution. Neither did the cheese prepared from the milk of these animals contain mercury. The author shows that, from the amount of mercuric chloride injected, the flesh at the utmost cannot contain more than 0.000018 gram of mercury per kilo.

W. P. S.

Use of Hydrogen Peroxide in Volumetric Analysis. SCHLOSSBERG (*Zeit. anal. Chem.*, 1902, 41, 735—747).—*Manganese*.—A manganese salt in presence of an alkali reduces an equivalent quantity of hydrogen peroxide with formation of manganese dioxide, which, on acidifying with sulphuric acid, reduces a second equivalent of the peroxide. An estimation of the excess of peroxide by titration with permanganate gives, therefore, the amount of manganese present. If much alkali chloride is present, this must be converted into sulphate by evaporation with sulphuric acid. In presence of large quantities of iron salts, the results are only approximate.

Lead.—The active oxygen in red lead and lead dioxide can similarly be estimated by hydrogen peroxide, by acidifying first with nitric acid and adding sulphuric acid before titration. Lead salts are therefore precipitated with bromine in presence of alkali, and the dioxide estimated as above. The presence of copper does not influence this mode of estimation. If other heavy metals are present, the lead is first precipitated as sulphate, which is dissolved in hydrochloric acid before adding potash and bromine.

M. J. S.

Estimation of Manganese. HENRI BAUBIGNY (*Compt. rend.*, 1902, 135, 965—967).—When manganese is precipitated as peroxide by means of a persulphate, it tends to carry down with it other salts present in the solution. This applies to alkalis particularly, and, in a large measure, may be avoided by working in acid solution. The process recommended is to acidify with 2 c.c. of concentrated sulphuric acid per 100 c.c. of liquid, then add ammonium persulphate solution, and heat on the water-bath until the evolution of oxygen slackens. If a trace of permanganate is formed, 4 or 5 drops of alcohol should be added to the cold solution. The precipitated peroxide is filtered off, washed, dried, ignited, and weighed as Mn_2O_4 .

J. McC.

Separation of Alkalis from Manganese Dioxide. HENRI BAUBIGNY (*Compt. rend.*, 1902, 135, 1110—1113. Compare preceding abstract).—It has already been shown that when manganese is precipitated by ammonium persulphate in presence of alkali salts the precipitate constantly contains an admixed impurity which cannot be removed entirely by washing with water. It has now been proved that the impurity is free alkali and can be removed entirely by washing the precipitate with a moderately concentrated solution of an ammonium salt (the nitrate).

J. McC.

Standardisation of Potassium Permanganate by Means of Oxalates. DUPRÉ, jun., and E. MÜLLER (*Zeit. angew. Chem.*, 1902, 15, 1244—1246).—The authors have experimented with the various oxalates and double-oxalates proposed from time to time, and state that the results nearest to the truth are obtained by using sodium oxalate (Sörensen) and lead oxalate (Stolba). In carrying out these experiments, a permanganate solution was used which had been standardised, according to Treadwell's directions, by means of electrolytically deposited iron.

L. DE K.

Analysis of Iron. NASKE (*Chem. Centr.*, 1902, ii, 1343; from *Stahl u. Eisen*, 22, 1134—1136).—The method of estimating carbon in iron or steel by dissolving the sample in solution of cupric ammonium chloride or iodine and burning the residue in a current of oxygen is too troublesome, and the author prefers the moist combustion with chromic and sulphuric acids. Phosphorus is best estimated as ammonium phosphomolybdate. In estimating sulphur, the author considers that the volatile organic sulphur compounds remain in the chlorinating liquid and do not collect in the wash-bottle containing the sodium hydroxide. It is inadvisable to pass the sulphurous gases into solution of silver nitrate, as this is also precipitated by hydrogen compounds of arsenic, phosphorus, and silicon.

L. DE K.

Analysis of Iron. FELIX BISCHOFF (*Chem. Centr.*, 1902, ii, 1343; from *Stahl u. Eisen*, 22, 1136—1139).—A reply to Naske (preceding abstract). The author considers the cupric ammonium chloride or iodine method the safest for the estimation of the carbon. The phosphorus in the yellow phosphomolybdate precipitate varies from 1.27 to 1.75 per cent. In estimating sulphur, the volatile organic sulphur compounds are not retained by the chlorinating liquid, but their sulphur will be found in the alkaline solution of sodium hypochlorite. No arsenic hydride is evolved when dissolving the sample in dilute hydrochloric acid, and the silver process of estimating sulphur is preferable to the estimation as barium sulphate.

L. DE K.

Modification of the Thiosulphate Method for the Volumetric Estimation of Iron. A. E. HASWELL (*Zeit. angew. Chem.*, 1902, 15, 1265—1267).—In reply to Gintl (*Abstr.*, 1902, ii, 429), the author refers to his process (*Rep. anal. Chem.*, 1881). This is a modification of Oudemans's method (titration of ferric iron with sodium thiosulphate in the presence of a little copper sulphate with potassium thiocyanate as indicator), in which excess of sodium salicylate is used as indicator, care being taken that the solution does not contain too much free hydrochloric acid. The unavoidable excess of thiosulphate may, if desired, be checked by means of standard solution of potassium dichromate or ferric chloride.

L. DE K.

Estimation of the Hardness of Potable and Service Waters by Aqueous Soap Solution. A. GAWALOWSKI (*Zeit. anal. Chem.*, 1902, 41, 748—752).—Instead of an alcoholic solution of a normal soap, a clarified aqueous solution of basic sodium oleate is employed, obtained by diluting a neutral sodium oleate solution until the acid salt separates. This solution gives a dense and very permanent froth, and if it is coloured by carmine tincture the contrast between the milky-white lather and the rose-coloured liquid indicates the end of the titration sharply. For technical work, neutral cocoanut oil soap may be used. The solution is standardised with four calcium chloride solutions of 20°, 10°, 6°, and 2° respectively (1° German = 10 mg. of CaO per litre), using of the first 25 c.c., of the second 50 c.c., of the third 75 c.c., and of the fourth 100 c.c. The same quantities of waters approximating to the respective standards in hardness are also taken. The reaction is

assumed to take place uniformly according to the equation
 $\text{Na}_4\text{C}_{36}\text{H}_{132}\text{O}_5 + 2\text{CaCl}_2 = 4\text{NaCl} + \text{Ca}_2\text{C}_{36}\text{H}_{132}\text{O}_5.$ M. J. S.

Combustion of Methane and Hydrogen by Winkler's Method. K. W. CHARITSCHIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 710—711).—Just as with mixtures of hydrogen and isopentane and of hydrogen and carbon monoxide (see Abstr., 1902, ii, 702), the author finds that when it is attempted to burn away the hydrogen from a mixture with methane by means of palladinised asbestos an appreciable part of the latter gas always undergoes combustion. In this case, however, the temperature at which the hydrogen burns is not raised, as is the case with the mixtures previously examined, so that the combustion of the methane must be due to the great heating effect of the burning hydrogen, which raises the temperature of the mixture locally to that at which methane burns. T. H. P.

Separation of Mineral Oil from Oil of Turpentine and Resin Oil. HERMANN HERZFELD (*Zeit. öffentl. Chem.*, 1902, 8, 446—447).—Ten c.c. of oil of turpentine are placed in a flask surrounded by a water-jacket and having ground into its neck a graduated cylinder fitted with a tap. Fifteen c.c. of fuming nitric acid are added to the turpentine drop by drop from the cylinder with constant shaking. The gases formed escape by a side opening in the stopper of the flask. The mixture is then transferred to the upper cylinder and the separated mineral oil read off, or weighed after washing with a little nitric acid and then with cold water. Mineral oil in resin oil may also be estimated by this method, more care, however, being required to prevent violent reaction between the oil and nitric acid, and consequent loss. W. P. S.

Detection of Resin Oil in Mineral Oils. GEORGES HALPHEN (*J. Pharm. Chim.*, 1902, [vi], 16, 478—483. Compare Abstr., 1902, ii, 293).—Resin oil gives an intense violet colour on treatment with phenol and bromine in carbon tetrachloride or light petroleum solution. Most vegetable and many animal oils give similar, but less intense, tints, mineral oils giving a brown colour with at most a violet reflex. The presence of water or alcohol prevents or hinders the reaction. The test is applied by moistening a porcelain dish with a solution of one drop of oil in 2 c.c. of a reagent composed of 1 part of absolute phenol in 2 of carbon tetrachloride, and allowing bromine vapour to descend evenly over the surface from a solution of bromine (1 vol.) in carbon tetrachloride (4 vols.); the colour is developed in from 5 to 10 seconds.

The oils may be divided into four classes: (1) Those giving an intense reaction: violet, resin; carmine mixed with blue or violet, resin, and Chinese wood oil (the latter often gives emerald-green); pure carmine, changing to ill-defined violet, marine animal oils. (2) Those giving well-marked, but less intense, reaction: carmine, animal oils, arachis, butters, and lanoline. (3) Those giving two less intense colour zones, the upper violet, the lower blue; linseed and hemp. (4)

Those giving very feeble or ill-defined tints ; in general, all other vegetable oils.

Details of the colours produced by a large number of specific oils are given in the paper.
G. D. L.

Digester-lixiviator for Testing Gutta-Percha. MAURICE PONTIO (*Ann. Chim. anal.*, 1902, 7, 450—452).—An apparatus by means of which four samples may undergo a preliminary extraction by being placed in contact with the boiling solvent (alcohol, chloroform, toluene). The vapour passes through four pear-shaped glass vessels placed one above the other and each containing a sample already partly exhausted. 0.5 gram of gutta-percha finely cut up is placed on a weighed filter which is inserted in a perforated funnel, which is then suspended in the extracting vessel. For details of construction, the drawing in the original paper should be consulted.
L. DE K.

Estimation of Glycerol in Wine. J. AUGUSTE TRILLAT (*Compt. rend.*, 1902, 135, 903—905).—Of the substances left on evaporating wine, cold ethyl acetate dissolves only the glycerol. In order to estimate the glycerol, 50 c.c. of wine are evaporated at 70° in a silver basin to one-third of this volume, and then, after addition of animal charcoal, the evaporation is carried to dryness ; to the residue, 5 grams of calcium oxide are added and the mixture extracted twice by thoroughly shaking with 30 c.c. of cold ethyl acetate free from alcohol ; on evaporating the extract, nothing but glycerol remains.

K. J. P. O.

Estimation of Pentoses. RICHARD JÄGER and ERNST UNGER (*Ber.*, 1902, 35, 4440—4443).—Counciler's method (*Chem. Zeit.*, 1894, 18, 966) has been employed for the estimation of furfuraldehyde from the following substances : furfuraldehyde, pure arabinose, gum from linseed, pine-wood, black and white pepper. The substance was distilled with hydrochloric acid, the distillate condensed with phloroglucinol, and the product analysed. With pure furfuraldehyde, the analytical data obtained agreed with the formula $C_{11}H_8O_4$, but in all the other cases the percentage of carbon was too low, and that of the hydrogen too high, owing to the presence of some impurity. It follows that the amounts of pentoses found by Counciler's method are too high.

J. J. S.

Densimetric Estimation of Sugar [in Urine]. TH. LOHNSTEIN (*Chem. Centr.*, 1902, ii, 1075 ; from *Apoth.-Zeit.*, 17, 664).—A slight modification of Roberts's formula used in his densimetric estimation of sugar in urine. The formula proposed is $p = f(s - s_0)$, in which p represents the percentage of sugar, s the density of the urine before fermentation, s_0 the density after fermentation, and f a constant to which, in practice, the value 221 may be assigned.
L. DE K.

Application of the β -Naphthylhydrazones to the Detection and Separation of the Sugars. ALBERT HILGER and S. ROTHENFUSSE (*Ber.*, 1902, 35, 4444—4447. Compare *Abstr.*, 1902, ii, 479).—*Xylose- β -naphthylhydrazone* crystallises from a mixture of methyl

alcohol and chloroform or benzene in greenish-yellow nodules and melts at 123—124°. *Lævulose-β-naphthylhydrazone* separates in yellow crystals when chloroform or benzene is added to its alcoholic solution and melts at 161—162°. The solubility of these hydrazones in alcohol affords a ready method of separating xylose and lævulose from other sugars.

The physical data of the hydrazones given by de Bruyn and Alberda van Ekenstein (*Abstr.*, 1896, i, 588) differ somewhat from those obtained by the authors. The difference is due to impurities and not to stereoisomerism.

R. H. P.

Calculation of Real Sugar in Chocolate. ALEXANDRE LEYS (*J. Pharm. Chim.*, 1902, [vi], 16, 471—474).—Five and ten grams of chocolate are separately dissolved in water, precipitated with basic lead acetate, made up to 100 c.c., and the rotations, α and α' , of each determined. The real amount of sugar in 10 grams (Q_1) is then calculated by the formula $Q_1 = 0.752 \left(\frac{\alpha\alpha'}{\alpha' - \alpha} \right)$.

G. D. L.

Estimation of Raffinose. G. WISKE (*Zeit. Ver. deut. Zuckerind.*, 1902, 562, 945—948).—The employment of animal charcoal for classification in the estimation of raffinose in sugar products by the inversion and polarisation method leads to a high value being obtained for the raffinose, and this the author shows to be due to the relatively large absorption of the melibiose formed on hydrolysing the raffinose. In the experiments made, the charcoal used was a sample of bone black extracted with hydrochloric acid, obtained from the laboratory of the German Sugar Industry Union, and taking the half normal weight of sugar (13.024 grams) per 100 c.c., the corrections to be applied to the polariscope readings, after inversion, for different percentages of raffinose found are: for 3 per cent. of raffinose, +0.1°; 4 per cent., 0.2°; 5 per cent., 0.3°, and 0.1° for each per cent. of raffinose up to 14.

T. H. P.

[Action of Alkaline Sugar Solutions on Potassium Cyanide.] TH. SCHUMACHER (*Zeit. Nahr. Genussm.*, 1902, 5, 1099—1105).—The mixture of various alkaline sugar solutions with potassium cyanide caused a considerable loss of hydrogen cyanide to take place, dextrose having the most pronounced action. After 8 days, a mixture of equal parts of $N/2$ potassium cyanide solution and 10 per cent. alkaline dextrose solution showed only traces of cyanide when tested, and had no poisonous action on rabbits. Milk, flesh, and solutions of albumin had the same action on potassium cyanide as sugars.

W. P. S.

Analysis of Blast Furnace Dust. LEOPOLD SCHNEIDER (*Chem. Centr.*, 1902, ii, 1161; from *Oesterr. Zeit. Berg.-Hütt.*, 50, 498).—The aqueous solution of this dust contains potassium ferrocyanide, thiocyanate, and cyanide; also potassium hydroxide, carbonate, and chloride. On adding silver nitrate to the strongly alkaline solution, the ferrocyanide is precipitated, and from the amount of metallic silver or ferric oxide obtained from the precipitate, the potassium ferrocyanide

may be calculated. On acidifying the filtrate with nitric acid, the other cyanides are thrown down. The precipitate from an aliquot part of the first filtrate is oxidised with nitrohydrochloric acid, the solution is diluted and filtered, and the sulphur (thiocyanate) is estimated as barium sulphate. Another part of the filtrate is also precipitated with nitric acid and the precipitate heated for an hour in the boiling water-bath with 200 c.c. of water and 10 c.c. of nitric acid of sp. gr. 1.2. This dissolves silver cyanate, which is then estimated as chloride. The precipitate obtained with a third portion of the filtrate from the ferrocyanide precipitate is boiled for an hour with an equal volume of strong nitric acid, diluted with an equal volume of water, and filtered. The silver which has passed into the solution represents cyanate, thiocyanate, and cyanide.

L. DE K.

Reduction of Ammoniacal Silver Solutions by Organic Substances. GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT (*J. Soc. Chem. Ind.*, 1902, 21, 1373—1375).—The results of the experiments emphasise the necessity of caution in employing the well-known reaction for formic and tartaric acids and the aliphatic aldehydes. A list of substances, divided into twelve groups, is given, the majority of which reduces silver solutions. Reduction occurs with aromatic mono- and di-amines, morphine, anthracene, sulphinic acids, phenols (mono-, di-, and tri-hydric), carbonyl derivatives, aminoazo-derivatives, uric acid, and glycerol (under certain conditions). The action is, however, only slight with the nitro- and carboxyl-derivatives of the phenols, thionaphthols, thiophen, naphthalene, and unsaturated compounds (turpentine, &c.).

W. P. S.

Estimation of Lactic Acid in the Volatile Acids of Wine. ALFRED PARTHEIL (*Zeit. Nahr. Genussm.*, 1902, 5, 1053—1062).—A part of the lactic acid occurring in wine is found with the volatile acids and cannot be separated from acetic acid by distillation (compare Abstr., 1901, ii, 700). The following method is given for the estimation of lactic acid in the presence of volatile acids. The dry barium salts are placed in a small flask provided with an india-rubber stopper, through which pass a tap-funnel and a delivery tube. The latter is connected with a nitrometer filled with potassium hydroxide solution. A little concentrated sulphuric acid is run into the flask and the latter is heated. The carbon monoxide formed is collected in the nitrometer, small amounts of sulphur dioxide and carbon dioxide, which are also evolved, being absorbed by the potassium hydroxide. The decomposition of the lactic acid proceeds according to the formula $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H} = \text{CH}_3 \cdot \text{COH} + \text{H}_2\text{O} + \text{CO}$. The number of c.c. of carbon monoxide, reduced to 0° and 760 mm. pressure, multiplied by 0.0012507 gives the weight of carbon monoxide, and on multiplying this by 3.126 the amount of lactic acid is found. The quantity of the latter present in the volatile acids of wine is about 0.04 per cent.

W. P. S.

Estimation of Tannic Acid by Ferric Salts. RUOSS (*Zeit. anal. Chem.*, 1902, 41, 717—734).—The official method of estimation by hide powder is open to the objection that the hide is capable of ab-

sorbing large amounts of acid dyes, such as chestnut brown, which may be used for the adulteration of tanning materials, and that it is liable in some cases to give results far above the truth. The following process yields a normal ferric tannate, which on ignition leaves pure ferric oxide, from which the amount of tannic acid can be calculated by multiplying by 4.024. The solutions required are (1) a $N/2$ solution of sodium carbonate, (2) a ferric solution (sulphate or chloride) slightly above $N/2$ strength, (3) acetic acid of $6N$ strength containing 5 grams of sodium tartrate per litre. When equal volumes of (1) and (2) are mixed, the filtrate from them must not be alkaline. Fifty c.c. of the tannic acid solution, of strength not exceeding 0.4 per cent., are mixed with 10 c.c. of solution (1), then 10 c.c. of solution (2), then immediately with 25 c.c. of solution (3), and well shaken. The mixture may then be boiled, which accelerates the reaction. After boiling for a minute, the precipitate is collected on a filter, washed with hot water until free from iron, dried, and ignited. Ferric gallate, being soluble in normal acetic acid, is not precipitated under these conditions.

M. J. S.

Detection of Heated Milk by means of Methylene Blue. FRANZ SCHARDINGER (*Zeit. Nahr. Genussm.*, 1902, 5, 1113—1121).—The reagent employed consists of a mixture of 5 c.c. of a saturated alcoholic solution of methylene blue, 5 c.c. of a 40 per cent. solution of formaldehyde, and 190 c.c. of water. One c.c. of this reagent is mixed with 20 c.c. of milk in a test-tube 18 cm. in length and 1.5 cm. in diameter, the tube being then placed in water heated at 45—50°. Raw milk decolorises the solution in about 10 minutes, whilst heated milk has no action on the colour. The critical temperature is about 80°. A similar reagent, but without the formaldehyde, is sometimes decolorised by raw milk.

W. P. S.

Detection of Heated Milk by means of the Guaiacum Test. EW. WEBER (*Milch. Zeit.*, 1902, 31, 657—659, and 673—676).—The test recommended by Arnold (*Abstr.*, 1902, ii, 539) was found to be simple and trustworthy. About 10 per cent. of heated milk can be detected in raw milk. The limit of temperature is about 80°. Ordinary preservatives, present in the quantities usually employed, have no influence on the test, but an excessive amount of formaldehyde interferes with the formation of the blue ring. The test is applicable to sour milk, curds, whey, and goats' milk. Raw asses' milk gives no blue ring. Tincture of guaiacum wood yields the best results and keeps well.

W. P. S.

Fats with Double Melting Points. HANS KREIS and AUGUST HAFNER (*Zeit. Nahr. Genussm.*, 1902, 5, 1122—1124).—On repeatedly crystallising lard, beef-fat, and mutton-fat from ether, products were obtained which, after treatment with Hübl's solution to remove small quantities of olein and recrystallising from ether, gave the following results. The lard crystals melted to a clear liquid at 51.2°; on further heating to 53°, this became opaque and solid, only becoming clear again at 66.0°. Beef-fat crystals first melted at 51.5°, became opaque at 53°, and were quite clear at 61.9°. Mutton-fat crystals melted at

52.3°; at a slightly higher temperature, they became solid and again melted at 62.3°. Recrystallising from ether, amyl alcohol, and a mixture of benzene and alcohol had no effect on the melting points.

W. P. S.

Estimation of Oil in Linseed. ALBERTO GOETZL (*Chem. Centr.*, 1902, ii, 1158; from *Oesterr. Chem. Zeit.*, 5, 413).—In extracting linseed, light petroleum is recommended instead of ether as it dissolves less cholesterol and linolin. Donath's reaction is not characteristic for resins only, as it is also obtained distinctly with linolin.

L. DE K.

[Detection of Sesamé Oil in] Earthnut Oil, &c. J. SCHNELL (*Zeit. Nahr. Genussm.*, 1902, 5, 961—963).—Equal portions of the oil and stannous chloride solution (German Pharmacopœia strength) are shaken in a test-tube and the latter placed in boiling water until its contents have separated. A pink coloration indicates the presence of sesamé oil. The test is particularly applicable in the case of margarines coloured with methyl-orange or some other tropœolin, the extraction of these colours with hydrochloric acid before applying the test being unnecessary. The author also mentions that East Indian samples of earthnut oil give iodine values as high as 95.0, this value being considerably above that usually ascribed to earthnut oil.

W. P. S.

Lecithin in Fats and Oils. HERMANN JÄCKLE (*Zeit. Nahr. Genussm.*, 1902, 5, 1062—1077).—Lecithin is not present in the free state in animal or vegetable life, and is an accidental constituent of fats and oils. Vegetable seeds yield oils containing the most lecithin, and the difference between animal and vegetable fats in this respect may be of some analytical use. Butter fat contains no lecithin, although this occurs in milk. The simplest way of estimating lecithin in fats is the basic combustion method.

W. P. S.

Estimation of the Nitrogenous Constituents of Urine by means of Mercuric Chloride. ERNST FREUND and RICHARD FELLNER (*Zeit. physiol. Chem.*, 1902, 36, 401—406).—Fifty c.c. of urine are rendered just acid with hydrochloric acid, using 5 drops of a 1 per cent. solution of sodium alizarinsulphonate as indicator. A sufficient quantity of saturated mercuric chloride solution is then added, the amount required being previously ascertained by adding the solution to a known volume of the urine until a drop tested with sodium carbonate gives a yellow precipitate. After removing free hydrochloric acid from the urine solution by the addition of a little sodium acetate solution containing acetic acid, the precipitate of uric acid and xanthine bases is filtered off. Creatine and ammonia are precipitated in the filtrate by the addition of an equal volume of a 50 per cent. sodium acetate solution. This precipitate is dissolved in hydrochloric acid and divided into two portions; in one, the total nitrogen is estimated. The other portion is rendered alkaline with potassium hydroxide and potassium iodide

is added, which causes the ammonia to be thrown down as oxydi-mercuriammonium iodide. After filtration, the filtrate is treated by Kjeldahl's method. A portion of the filtrate from the creatine-ammonia precipitate is treated with hydrochloric acid in the proportion of 3.5 c.c. of acid to 10 c.c. of saturated mercuric chloride solution, the amount of mercury in the solution having been previously estimated by titration with potassium cyanide and silver nitrate. The acid solution is then precipitated with an excess of sodium carbonate, an insoluble compound of urea and mercury being formed. Should the urine contain albumin, this must be removed by boiling the feebly acid solution before the first precipitation with mercuric chloride. Peptones, urobilin, albumoses, and alloxuric substances are thrown down in the creatine precipitation. The presence of sugar has no influence on the process. W. P. S.

Estimation of Urea by the Hypobromite Process. H. J. PECHELL (*Brit. Med. J.*, 1903, i, 194).—It has been stated that in diabetic urine the urea yields nearly the normal amount of nitrogen in the hypobromite process. It is now found that although the addition of dextrose to solutions of pure urea has no influence, the addition to normal urine has the same effect as in diabetic urine.

W. D. H.

Colour Reaction for *p*-Toluidine. JOACHIM BIEHRINGER and ALBERT BUSCH (*Chem. Zeit.*, 1902, 26, 1128—1129).—When to a slightly acid solution of *p*-toluidine in hydrochloric acid a few drops of ferric chloride are added, the mixture assumes a Bordeaux-red colour, slowly in the cold, but rapidly on boiling. If aniline or toluidine is also present, a bluish-green precipitate is formed, whilst the filtrate is red. The reaction is so sensitive that traces of *p*-toluidine may be detected in "pure" specimens of aniline and *o*-toluidine.

L. DE K.

Quantitative Separation of Leucine and Tyrosine. JOSEF HABERMANN and R. EHRENFELD (*Zeit. physiol. Chem.*, 1902, 37, 18—28).—A mixture of leucine and tyrosine is readily separated by the aid of boiling glacial acetic acid, in which the leucine is fairly readily soluble. The two substances may then be further purified by crystallisation from alcohol or water. The leucine obtained in this way from casein melted and decomposed at 270° (uncorr.) either in an open or a closed tube; the tyrosine melted and decomposed at 272° (uncorr.) in an open tube, but at 265° (uncorr.) in a closed tube.

The solubilities in glacial acetic acid are: leucine at 16°, 10.9; at 117°, 29.23; tyrosine at 16°, 0.14; at 117°, 0.18. The separation is practically quantitative when 0.5—1.0 gram of the mixture is heated just to boiling with 10 c.c. of glacial acetic acid and 10 c.c. of 95 per cent. alcohol.

J. J. S.

General and Physical Chemistry.

Abnormal Changes in some Lines in the Spectrum of Lithium. HUGH RAMAGE (*Proc. Roy. Soc.*, 1903, 71, 164—171).—The flame, spark, and arc-light spectra of lithium have been examined, and the results compared with those obtained by other observers. The lines in the principal series broaden and reverse quite normally. In the second subordinate series, the lines do not reverse even in the arc, but they may be caused to broaden towards the less refrangible end of the spectrum. In the first subordinate series, the lines broaden more rapidly on the more refrangible side of the spectrum. In intense arcs, the inner cone, and in weak arcs and sparks the parts near the negative pole, give a broad reversed line with its centre about wavelength 4603.07, which coincides with the lines in the spectra of the oxyhydrogen flame and of the uncondensed spark. The true lithium lines are those which occur in the spectrum in the oxyhydrogen flame.
J. McC.

Emanation-substance from Pitchblende and Radium. FRITZ GIESEL (*Ber.*, 1903, 36, 342—347. Compare this vol., ii, 20).—A substance can be isolated from pitchblende which is quite free from radium and thorium, but yet gives off a powerful emanation; this emanation, unlike that from thoria, does not decrease in intensity with time (compare Rutherford and Soddy, *Trans.*, 1902, 81, 837). The chloride crystallises well, phosphoresces and emits the emanation; the sulphate does not exhibit these properties. The main impurity in this specimen seems to be lanthanum salts. The Becquerel radiation of this substance has about the same intensity as that of radium. A series of experiments has shown that the velocity of the emanation in an electric field is increased when it moves in a direction from a positive to a negative electrode, and is decreased when it moves in the opposite direction. The emanation must therefore carry a positive charge. The name E-radiation is suggested for the radiation of this substance.

It has been shown by Runge and Bodländer that the gas evolved by a solution of radium bromide is hydrogen.
K. J. P. O.

Luminescence of Gases. ALEXANDER DE HEMPTINNE (*Bull. Acad. Roy. Belg.*, 1902, 11, 775—795).—The paper contains data on the connection between the nature of the gas, the pressure, and the electrical conditions required to induce luminescence under the influence of electric waves. Hydrogen, ammonia, acetylene, carbon monoxide, nitrogen, oxygen, carbon dioxide, and carbon disulphide, and mixtures of hydrogen and acetylene were examined. The chemical changes caused by the electric waves in gaseous mixtures were studied. Carbon disulphide appears to be decomposed more quickly than

ammonia in a mixture, but the reaction is probably complicated, thiocyanates being formed. The decomposition of carbon disulphide is also greater in the presence of hydrogen than of nitrogen; this the author considers to be due to emission of more "electric corpuscles," which favour the decomposition, by hydrogen than by nitrogen. G. D. L.

Radioactivity from Rain. C. T. R. WILSON (*Proc. Camb. Phil. Soc.*, 1902, 12, 17).—A vessel, either of platinum or of porcelain, in which freshly fallen rain has been evaporated to dryness exhibits radioactivity for a few hours, and the vessel may be heated to dull redness without destroying the effect. The character of the rain and the time of its fall are also immaterial, the only abnormally large effect being obtained from rain collected during a thunderstorm. If a precipitate is produced in the freshly fallen rain, either from barium chloride and sulphuric acid or from alum and ammonia, the radioactivity is associated with the precipitate, and the vessel in which the filtrate is evaporated remains inactive. From 190 c.c. of rain, a precipitate was obtained which increased the ionisation within a testing vessel to 100 times its normal value. Similar precipitates formed in tap water, or in rain water which has stood for twenty-four hours, are quite inactive. J. C. P.

Spontaneous Ionisation in Air at Different Temperatures and Pressures. J. PATTERSON (*Proc. Camb. Phil. Soc.*, 1902, 12, 44).—The experiments indicate that the spontaneous ionisation referred to is really due to easily absorbed radiation from the walls of the vessel. J. C. P.

Bipolar Electrodes with Insoluble Anodes. ANDRÉ BROCHET and C. L. BARILLET (*Bull. Soc. chim.*, 1903, [iii], 29, 73—77).—The term bipolar or interelectrode is used to describe a sheet of metal inserted between the anode and cathode of an electrolytic cell; the face of the interelectrode opposite to the cathode of the cell is called the interanode, and the second face the intercathode.

The bipolar electrode used consisted of a sheet of platinum immersed in the liquid, but not in contact with the walls, of a cell in which a solution of cupric sulphate was undergoing electrolysis between an anode and a cathode of copper. Under these conditions, the proportion of the current (indicated by the amount of copper deposited on the intercathode) which passes through the interelectrode is always small and dependent on the difference of potential at the cell electrodes, which must be greater than the tension of dissociation of the electrolyte, and on the relation between the surfaces of the bipolar electrode and the section of the cell, which must be nearly equal before any considerable proportion of the current passes through the former.

The potential difference for a given current strength is greatest when the interelectrode is placed midway between the electrodes. Displacement towards the anode gives rise to the deposition of a thickened circular deposit of small diameter, whilst displacement in the opposite direction leads to the formation of a thin, square deposit of larger surface.

When the insoluble interanode is made soluble by coating it with a layer of copper, the potential difference for the same current strength is reduced and the deposit on the intercathode is increased until the interanode copper is wholly dissolved. The potential difference then increases and the excess of the intercathode deposit is slowly dissolved, leaving, however, a circle of slightly larger diameter than that obtained under the usual conditions, after which the reaction proceeds normally. This displacement of the interanode copper film occurs even when the potential difference is less than the dissociation tension of cupric sulphate.

Where two platinum interelectrodes are used, disposed at equal distances from the cell electrodes and from each other, the requisite difference of potential is higher than where one is used, the deposit of copper is less and is unequally divided between the two intercathodes, that nearer the cell anode receiving more than that more remote.

T. A. H.

Bipolar Electrodes with Soluble Anodes. ANDRÉ BROCHET and C. L. BARILLET (*Bull. Soc. chim.*, 1903, [iii], 29, 77—82. Compare preceding abstract).—Assuming that a copper interanode exerts no special action in an electrolytic cell in which an acid solution of cupric sulphate is the electrolyte and also that the current flow is uniform, $w/W = s/S$, where w and W are the masses of copper deposited on the intercathode and cathode respectively and s and S the surfaces of the interelectrode and cell section respectively. Measurements, made by means of a separable bipolar electrode composed of two thin sheets of copper joined by caoutchouc bands, show that the deposition of copper on the intercathode is much less for weak currents and slightly less for strong currents than that required by the foregoing relation; the results are of the same order whether pure or impure copper is employed.

This difference is due to a small extent to ordinary polarisation effect, but principally to a phenomenon described as "resistance to current flow" or "back *E.M.F.*" of the kind observed by Poggendorf, Lechner, Lenz, Bary, and others in the investigation of electrodes with soluble anodes. The author prefers to regard the effect as due to a variable "back *E.M.F.*," since if it were a resistance its relation to the current strength would be constant. The value a of the small polarisation effect, together with that due to this "back *E.M.F.*," is given by the relation $E' - E = (n-1)a$, where E' and E are respectively the *E.M.F.*'s of the cell, with and without n bipolar electrodes, dividing the cell completely into $(n+1)$ parts; it may amount to $E/10$ for the current strengths employed in practice.

T. A. H.

Employment of Bipolar Electrodes. ANDRÉ BROCHET and C. L. BARILLET (*Bull. Soc. chim.*, 1903 [iii], 29, 82—83. Compare preceding abstracts).—Interelectrodes with either soluble or insoluble anodes equally deflect the current flow; when used commercially, they should divide the cell completely into two or more parts and where mechanical agitation of the electrolyte is necessary they should be enclosed in frames. The results recorded in the two preceding

abstracts show that no loss results from the use of wooden vats lined with lead in "wet" electrometallurgical processes.

T. A. H.

Reduction of Insoluble Cathodes. ALFRED T. WEIGHTMAN (*J. Physical Chem.*, 1903, 7, 18—28).—The reduction of lead sulphate requires a higher voltage than the liberation of hydrogen, yet little hydrogen is evolved in charging a storage cell until practically all the lead sulphate is reduced. In the electrolytic process for the reduction of lead sulphide, the difference between the thermal values of lead and hydrogen formation is very considerable, and it is remarkable that notwithstanding this a high reduction-efficiency is obtained. The efficiency is dependent largely on the purity and fineness of division of the ore, but is independent of the current density. The ore, however, cannot be completely reduced, about 5 per cent. of lead sulphide always remaining. Examination of the gases evolved shows that oxygen is present in only small quantities; this is, perhaps, due to oxidation of the hydrogen sulphide to oxy-sulphur compounds. Experiments were also made with cuprous and nickel sulphides. The explanation of these results may be that the voltage required to liberate hydrogen is not constant but dependent on the metal constituting the cathode.

L. M. J.

Behaviour of a Potassium Amalgam Cathode in a Vacuum Tube. THEODORE LYMAN (*Proc. Camb. Phil. Soc.*, 1902, 12, 45—46).—The potential difference necessary to send a discharge through air at low pressures is less when a potassium amalgam is used as cathode than when pure mercury is employed.

J. C. P.

Electromotive Force of Alloys of Tin, Lead, and Bismuth. E. S. SHEPHERD (*J. Physical Chem.*, 1903, 7, 15—17).—The *E.M.F.* of alloys of bismuth and tin measured against pure tin is exceedingly small, being little greater than that of one sample of tin against another, so that tin and bismuth separate pure from the melt and form no solid solution. Lead and bismuth alloys measured against lead, however, give an *E.M.F.* which increases as the amount of bismuth increases to about 10 per cent., and then remains constant until the percentage reaches about 90, after which it increases to the value for pure lead. This accords with a system giving two solid solutions; at first, a variable single solid phase is present, then from 10 to 90 per cent. bismuth, two solid phases of constant composition, and afterwards one variable solid phase. The results, therefore, completely confirm the author's previous experiments (this vol., ii, 77).

L. M. J.

The Hall Effect and the Speed of Ions of a Salt Vapour. GEORGES MOREAU (*Compt. rend.*, 1902, 135, 1326—1328. Compare this vol., ii, 125).—By the method previously described, it has been found that the speed of the negative ion diminishes as the concentration of the salt increases, and is dependent solely on the nature of the metal. For potassium and sodium salts, when the solution vaporised is N to $N/256$, the speed varies from 660 to 1320 cm. per second for a fall of potential of 1 volt per cm.

The same method gives as the speed of the positive ion 80 cm. per

second for a fall of 1 volt per cm., whatever be the nature or concentration of the salt.

The rotation-coefficient of the Hall effect is measured, according to Marx, by the difference of these speeds. This has been experimentally verified.

The author concludes that the negative ion consists of a nucleus produced by the disruption of the metallic atom to which are attached other non-ionised atoms, increasing in number with the concentration. The positive ion would be formed of the rest of the atom along with the molecules of the surrounding medium. This explains the predominating influence of the metal on the conductivity of salt vapours as observed by Arrhenius. J. McC.

Magnetisation of Liquids with Change of Temperature. G. PIAGGESI (*Nuovo Cim.*, 1902, [v], 4, 247—269).—From the results of experiments made on water and on aqueous solutions of various concentrations, of salts of iron, manganese, cobalt, and nickel, the author draws the following conclusions: (1) for water, the diamagnetism diminishes with rise of temperature, of which it is a linear function. (2) The magnetic susceptibility of water for temperatures between 23° and 86° follows the law:

$$k = -0.804(1 - 0.00175t)10^{-6},$$

t being the temperature. (3) The magnetic susceptibilities of solutions decrease as the temperature rises, the temperature coefficients for the solutions examined being almost identical and of the same order of magnitude as the coefficient of expansion of gases. (4) The product, $\theta.k.10^{-6}$, of the magnetic susceptibility and the absolute temperature is a constant, the value of which depends only on the nature and concentration of the solution, as has been previously found for oxygen and for aqueous ferrous sulphate; this product diminishes with the concentration of the solution. T. H. P.

Thermochemistry of Metaphosphoric Acid. H. GIRAN (*Compt. rend.*, 1902, 135, 1333—1335).—The heat developed by the transformation of metaphosphoric acid into orthophosphoric acid was measured, the change being brought about by means of sulphuric acid. The result obtained was:

HPO_3 (solid) + H_2O (liquid) = H_3PO_4 (solid) + 10.22 Cal. The heat of solution of solid metaphosphoric acid is +9.76 Cal.; the heat of solution of fused sodium metaphosphate is +3.97 Cal. The heat of neutralisation of dissolved metaphosphoric acid by sodium hydroxide is +14.84 Cal. From these results, the author further deduces:

HPO_3 (solid) + Na (solid) = NaPO_3 (solid) + H + 63.03 Cal. The corresponding reaction with pyrophosphoric acid gives 54.11 Cal., and that with orthophosphoric acid gives 49.38 Cal. The heat of formation of metaphosphoric acid from its elements is calculated to be +234.64 Cal., but this number is given with some reserve. J. McC.

Cinchona Alkaloids. [Thermochemistry of] Quinine and Quinidine. MARCELLIN P. E. BERTHELOT and GAUDECHON (*Compt. rend.*, 1903, 136, 128—139).—A complete investigation of the thermochemistry of quinine and quinidine has been made, and the

following results have been obtained. The heat of combustion of anhydrous amorphous quinine, $C_{20}H_{24}O_2N_2$, is 8216 Cal., and therefore the mol. heat of combustion 2661.3 Cal. The heat of formation from the elements is 50.5 Cal., and the heat of solution in dilute solution of 4HCl at 12° is +16.2 Cal. The heat of solution of crystallised quinine trihydrate in the same solution is +11.5 Cal., consequently the addition of $3H_2O$ to anhydrous quinine is accompanied by a development of +4.73 Cal. The heat of solution of freshly precipitated quinine in 4HCl solution differs from that of the anhydrous substance by +1.55 Cal., and this can be explained by assuming that the hydration of the quinine is slow. The heat of solution of precipitated quinine which has stood in contact with the mother liquor for 5 days is lower by 8.5 Cal. than that of anhydrous quinine, and this indicates that the hydration proceeds beyond $C_{20}H_{24}O_2N_2, 3H_2O$ to perhaps 8 or $9H_2O$; the difference may, however, be due to the quinine molecule undergoing some specific transformation. When dilute alkalis are added to quinine, no sensible heat change takes place. The heats of neutralisation with various acids have been determined: the anhydrous base with 4HCl (dilute) develops 16.2 Cal. at 11° and 15.5 Cal. at 19°, whilst with HCl at 11° it develops 9.9 Cal., therefore for the fixation of the first molecule of hydrogen chloride 9.9 Cal. are developed, and 6.3 Cal. for the second, the addition of more hydrogen chloride does not result in any further heat change. The values found for the heats of formation of the solid hydrochlorides are 11.9 Cal. for $C_{20}H_{24}O_2N_2, HCl$, and 20.8 Cal. for $C_{20}H_{24}O_2N_2, 2HCl$ from dissolved hydrochloric acid, and 29.3 and 55.2 Cal. respectively from gaseous hydrogen chloride. $C_{20}H_{24}O_2N_2, HCl + 2H_2O$ (liquid) = crystallised salt + 4.0 Cal.; $C_{20}H_{24}O_2N_2 + CH_3 \cdot CO_2H$ aq. = dissolved salt - 0.22 Cal.; the heat of neutralisation with solid acetic acid to give the solid salt would be +8.15 Cal. The heat of neutralisation with one mol. of lactic acid in dilute solution is +9.0 Cal. at 11°, and the heat of solution of the crystallised lactate is -1.83 Cal. With a dilute solution of one mol. of sulphuric acid, the heat developed is 18.7 Cal. at 12°, and with $2H_2SO_4$ it is 18.0 Cal. With one mol. of oxalic acid in dilute solution at 11°, quinine develops 16.3 Cal., and with $2C_2H_2O_4$ 15.2 Cal. The diacid salts are therefore formed endothermically. From a comparison of the results with those obtained with the alkalis, it is deduced that quinine is comparable in strength with these.

The heat of combustion of quinidine is 2660.6 Cal.; its heat of formation from the elements is +51.2 Cal. The heat of solution of the freshly precipitated quinidine in a dilute solution of 4HCl differs from that of the anhydrous base by 2.6 Cal. The heats of neutralisation with acids are very nearly the same as those of quinine.

J. McC.

Volumenometer for Small Quantities of Substance. LUDWIG ZEHNDER (*Ann. Physik*, 1903, [iv], 10, 40—71).—A small glass vessel of known displacement and internal capacity, containing a weighed quantity of the substance the density of which is to be determined, is introduced into a barometer tube, the upper end of which is closed

by a well-fitting stopper and mercury seal. A Torricellian vacuum having been formed and the air in the glass vessel allowed to pass into it, the height of the mercurial column is altered until the meniscus reaches a fixed point. The density can then be calculated from the height of the mercurial column. When the apparatus has been carefully calibrated, it is possible to obtain excellent results with very small quantities of substance (0.1—0.3 gram). The results obtained for the sp. gr. of a substance (1) when granular, (2) when powdered, are almost the same. The method has the additional advantage that the substance investigated is not brought into contact with any liquid.

J. C. P.

Modifications of Say's Stereometer. E. MAMELI and A. SANNA (*Gazzetta*, 1902, 32, ii, 211—214).—In place of the greased plate of Say's stereometer (*Ann. Chim.*, 1797, 23, 1), the authors employ a hermetically sealed cover provided with a vertical cock, which serves also as a handle. Also, instead of having two scales, the tube is furnished with only one, and is so adjusted that a length of two centimetres corresponds with a volume of 1 c.c. As immersion liquid, water is used in place of mercury. The apparatus is used in the same way as that of Say and gives more accurate results than the latter, as is shown by the results of a number of measurements of the volumes of definite quantities of water, flowers of sulphur, iron, mercury, paraffin, fused nickel, marble, granite, alum, asbestos threads, and rock salt.

T. H. P.

Influence of Pressure on the Propagation of Explosion in Gases. ALEXANDER DE HEMPTINNE (*Bull. Acad. Roy. Belg.*, 1902, 11, 761—775).—The limiting pressures, below which explosion caused by sparking or by incandescence does not occur, have been determined for various explosive mixtures. The values are rather variable, the mean pressures in mm. (the first figure for sparking, the second for incandescence) being: hydrogen, 35 and 192; carbonic oxide, 58 and 145; methyl alcohol, 45 and 145; ethyl alcohol, 40 and 125; ether, 35 and 125; benzene, 25 and 105; acetylene, 15 and 45; carbon disulphide, 12 and 14. The mean explosion temperature of the mixture ether—oxygen has been determined as 225°; acetylene—oxygen, 180°; and carbon disulphide—oxygen, 200°. No certain relationships can be traced between the explosion pressure, heat of formation, heat of combustion, explosion temperature, speed of explosion wave, and temperature of combustion, a tabular survey of which is given in the paper, but the explosion caused by sparking has a different character to that caused by incandescence; the chief factor in the first case appears to be the velocity of translation of the molecules, whilst in the second the heats of formation and combustion and the temperature of reaction play a predominant part.

No combination occurs on sparking a mixture of nitrogen and hydrogen under a pressure of 80 atmospheres, or in a mixture of acetylene and nitrogen under five or ten atmospheres. Under 30 atmospheres, the acetylene in the latter experiments decomposes into carbon and hydrogen.

G. D. L.

Metallic Substitution. ALB. J. J. VANDEVELDE and C. E. WASTEELS (*Bull. Acad. Roy. Belg.*, 1902, 11, 795—839).—The speed of reaction between pure zinc and aqueous and dilute alcoholic solutions of copper sulphate is shown to depend on the form of the metal, its position, and the state of rest or motion of the liquid. The presence of alcohol retards the initial solution of the zinc, but after a certain point increases it, so that more metal dissolves in the alcoholic than in the aqueous solution when in a state of rest, the difference disappearing in solutions which are agitated. In all cases, the solution of zinc continues after complete precipitation of the copper, and to a greater extent in the dilute alcoholic solution than in the aqueous, the amount of hydrogen evolved being consequently larger in the former than in the latter case. This is attributed to hydrolytic dissociation of the sulphates, in consequence of which zinc hydroxide is precipitated and can be detected in the deposit of copper. The second part of the paper [by C. E. WASTEELS] contains a mathematical discussion of the influence of the form of the reacting metal. G. D. L.

Rate of Oxidation of Ferrous Salts by Chromic Acid. CLARA C. BENSON (*J. Physical Chem.*, 1903, 7, 1—14).—The present paper contains an account of experiments on the reaction between chromic acid and ferrous sulphate in the absence of iodides, the results of similar experiments in the presence of potassium iodide being deferred. The estimation of ferrous salt in solutions containing also ferric salts, potassium dichromate, and sulphuric acid caused considerable difficulty, and was finally effected by measuring the rate of oxidation of potassium iodide by the mixture, the rate being increased by the ferrous salt. The experiments indicate that the rate of oxidation of ferrous sulphate is proportional to the second power of the concentration of both ferrous salt and acid. The variation of concentration of the dichromate did not lead to definite results, the increase of rate of oxidation being apparently proportional to the 1.7th power of the concentration. Ferric salts cause a great retardation.

L. M. J.

Principle of Chemical Equilibrium. (Isomeric Transformation of the α -Oxides of Olefines into Aldehydes and Ketones.) WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 918—934).—The author discusses the various explanations which have been put forward for the isomeric transformation of the oxides of α -glycols into aldehydes or ketones. Some of these are not in accordance with observed facts, and none of them explains the transformation of the oxides of pinacones into pinacolines.

According to the author's views, the oxide first combines with the acid present, and the compound thus formed then undergoes intramolecular rearrangement and afterwards loses the elements of the acid originally taken up. In this rearrangement, it is necessary to suppose that carbon radicles, like elementary atoms and groups, are capable of changing over from one carbon atom to another in the

molecule. An example of the method in which this change is carried out is :



T. H. P.

The Solubility Equilibrium between Silver Chloride, Silver Oxide, and Solutions of Potassium Chloride and Hydroxide.

ARTHUR A. NOYES and D. A. KOUR (*J. Amer. Chem. Soc.*, 1902, 24, 1141—1148).—The solubilities of silver oxide and silver iodate have been determined analytically ; for silver oxide, it is 2.16×10^{-4} gram-mol. per litre, and for silver iodate 1.89×10^{-4} gram-mol. per litre at 25° .

Excess of moist silver oxide and silver chloride was shaken with solutions of potassium hydroxide of definite strengths at 25° and the concentration of hydroxyl and chlorine ions in the solutions was determined. It is found that the ratio of the concentrations of chlorine and hydroxyl ions increases by only 8 per cent., when the concentration of the potassium hydroxide increases six times ; the value of the ratio is about 0.01. On the basis of the law of mass action, it is shown that this ratio indicates that the solubility of silver chloride is about one-tenth of that of the oxide. The solubility of silver chloride would therefore be 2.16×10^{-5} gram-mol. per litre ; this is only in tolerable agreement with the value, 1.5×10^{-5} , obtained by Kohlrausch and Rose from conductivity experiments, and the difference may be explained by the fact that in deducing the value 2.16×10^{-5} it was assumed that the silver hydroxide is completely dissociated. Inversely, using Kohlrausch and Rose's value, it is found that silver hydroxide in its saturated solution is only dissociated to the extent of 70 per cent.

J. McC.

Basis of the Theory of Solution. MATHIAS CANTOR (*Ann. Physik*, 1903, [iv], 10, 205—213).—A theoretical paper. Exception is taken to one of the assumptions involved in Planck's thermodynamical treatment of solutions, and the author develops a theory which, it is claimed, is entirely free from hypothesis.

J. C. P.

Oxidation of Ammonia and Amines by Catalytic Action.

J. AUGUSTE TRILLAT (*Compt. rend.*, 1903, 136, 53—56).—When ammonia is oxidised in presence of water vapour by means of a heated platinum wire, it yields nitrous acid, a smaller quantity of nitric acid, and a small amount of free nitrogen. Alkylamines and diamines, under similar conditions, yield nitrous and nitric acids and an aldehyde, as if the amine were first resolved into ammonia and an alcohol which were afterwards oxidised separately. Triethylamine is practically unaffected by air and water in contact with platinum. Aniline is likewise not oxidised under these conditions, but dimethylaniline is converted into the compound $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe}$, the alkyl groups being first attacked and partially converted into aldehyde, which brings about the condensation.

C. H. B.

The Number of Stereoisomerides. ZDENKO H. SKRAUP (*Ber.*, 1903, 36, 141. Compare this vol., ii, 67).—Piccinini (*Gazzetta*, 1900, 30, i, 125) has previously drawn attention to the effect of the connection of asymmetric carbon atoms by "bridge-linking" on the number of stereoisomerides. A. H.

An Automatic Gas Generator. HENRY H. DENHAM (*J. Amer. Chem. Soc.*, 1902, 24, 1080—1081).—A simple form of gas apparatus is described, in which the acid reservoir is so connected with the generator that the spent acid is returned to the bottom of the reservoir, whereas fresh acid is drawn off from the top. E. F. A.

Inorganic Chemistry.

The Proportion of Hydrogen in the Atmosphere. ANATOLE LEDUC (*Compt. rend.*, 1902, 135, 1332—1333).—In reply to Gautier's criticism (this vol., ii, 138) of the author's previous paper (this vol., ii, 68), it is noted that the density there referred to relates to atmospheric nitrogen free from hydrogen and hydrocarbons, these having been carefully removed. It is insisted that the copper used by Dumas and Boussingault in their analysis of air must have contained hydrogen, because they passed several litres of air over the heated copper, and this can only have removed the moisture. Hydrogen forms a stable compound with copper below a red heat, and its tension of dissociation only becomes appreciable at such a temperature as that at which the copper completely absorbs oxygen from the air. The author maintains the views previously expressed. J. McC.

The Proportion of Hydrogen in the Atmosphere. ARMAND GAUTIER (*Compt. rend.*, 1903, 136, 21--22).—A further reply to Leduc. C. H. B.

Decomposition of Hydrogen Peroxide by Electrolytic Oxygen or Hydrogen. SIMEON TANATAR (*Ber.*, 1903, 36, 199—202).—Two Hofmann's voltmeters are placed in circuit with a battery of 10 cells. In one voltmeter, 15 per cent. sulphuric acid is placed, and in the other a similar solution containing hydrogen peroxide. The volume of oxygen in the second voltmeter is always greater, and the volume of hydrogen less, than the volumes of the same gases in the first voltmeter. This undoubtedly indicates that hydrogen peroxide is oxidised at the anode and at the same time reduced at the cathode. With a 3 per cent. solution of the peroxide, the reaction at the anode

proceeds quantitatively according to the equation $O + H_2O_2 = H_2O + O_2$, and with a 6 per cent. solution the reduction at the cathode is practically quantitative and no hydrogen is evolved.

A solution of the peroxide, when electrolysed in presence of nitric acid, behaves in exactly the same manner. Comparatively strong solutions of sulphuric acid, when electrolysed, do not decompose the peroxide. Ozonised oxygen and hydrogen peroxide react but very slowly.
J. J. S.

Relative Strengths of Hydrochloric and Nitric Acids, and the Behaviour of the Latter towards Solutions of Potassium Iodide. OTTO KÜHLING (*Zeit. angew. Chem.*, 1902, 15, 1257—1261).—In order to determine whether any difference exists between the strengths of hydrochloric and nitric acids, the reaction between potassium dichromate and potassium iodide in the presence of hydrochloric and nitric acids, respectively, has been investigated. The amount of iodine set free was independent of the nature of the acid, and corresponded accurately with the amount of dichromate present. Potassium iodide appears to be very stable towards nitric acid; in a mixture containing 20 c.c. *N*/10 potassium dichromate, 40 c.c. *N*/10 potassium iodide, and 100 cm. nitric acid of sp. gr. 1·2, 20·5 c.c. *N*/10 iodine was found free after ten minutes; in the presence of an equivalent amount of hydrochloric acid, 20·5 c.c. *N*/10 iodine was also set free in the same time.
K. J. P. O.

Apparatus for the Liquefaction of Air and Hydrogen. KARL OLSZEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 619—633).—Experience has shown that Hampson's apparatus for liquefying air is far superior to Linde's. A modified Hampson's apparatus is described by means of which double the amount of air can be liquefied for the same expenditure of energy as is found possible with Hampson's original apparatus. In this apparatus, the details of the construction of which are given in the paper, the expanded and cooled air is used to cool the Hampson regenerator through which the expanding air is passing. A smaller apparatus, consisting of one Hampson regenerator, with which 100 cm. of liquid air can be obtained in 10 minutes, is also described.

The apparatus for liquefying hydrogen is of the Hampson type and differs from those devised by Dewar and Travers in the following points; the liquid air used to cool the hydrogen is boiled under the ordinary pressure; no means of cooling other than by means of liquid air is used; only three litres of liquid air are required to produce 200—300 cm. of liquid hydrogen, whereas Travers' apparatus uses 8 litres for the same amount. A detailed description of the apparatus (with diagrams) and of its method of working is given in the paper.

K. J. P. O.

Analyses of Air from Coal Mines. FREDERICK B. GUTHRIE and A. A. ATKINSON [and, in part, W. M. HAMLET] (*J. Roy. Soc. N. S. Wales*, 1902, 35, 52—61).—Examination of four samples of air from the return airway, Wallsend colliery, showed the absence of carbon monoxide and methane, a deficiency of oxygen of 0·85—1·59 per cent., and an excess of carbon dioxide of 0·16—0·28 per cent. (ordinary air

containing 20.9 per cent. of oxygen and 0.03 per cent. of carbon dioxide). In four samples from Burwood colliery, carbon monoxide and methane were absent; there was a deficiency of oxygen of 0.07—0.56, and an excess of carbon dioxide of 0.01—0.10 per cent.

Four samples of air were withdrawn from the Gunnedah mine, which had been sealed for the previous three months in order to extinguish an outbreak of fire; carbon monoxide and inflammable gases were absent, carbon dioxide was present to the extent of 1.04—2.09, oxygen, 13.68—16.93, and nitrogen, 82.03—84.23 per cent. Some years ago, the workings of Greta colliery were sealed on account of the occurrence of spontaneous fires. The composition of two samples of air from this mine was as follows; carbon dioxide, 2.14—2.17; oxygen, 10.50—10.60; and nitrogen, 87.23—87.36 per cent.

[With WILLIAM M. HAMLET.]—The composition of gases obtained from the Dudley colliery after it had been closed down in consequence of explosion and fires was determined. One sample consisted of 3.2 per cent. of carbon dioxide, and 96.8 per cent. of methane, whilst another sample contained 2.8 per cent. of carbon dioxide, 15.0 per cent. of atmospheric air, and 82.2 per cent. of methane. E. G.

Chlorides of Sulphur, especially the so-called Sulphur Dichloride. OTTO RUFF and GEORG FISCHER (*Ber.*, 1903, 36, 418—433).—Two preparations of the so-called sulphur dichloride, containing 70.1 and 71.9 per cent. of chlorine, were vaporised at the temperatures -10° and 0° respectively by the passage of a stream of carefully dried and cooled carbon dioxide; the composition of both the liquid and the vapours was determined by analysis, the latter by absorbing the gases in nitric acid containing silver nitrate. The composition of the liquid was determined at intervals by sucking up small quantities into exhausted glass bulbs and treating these by the Carius method, intermediate compositions being deduced by interpolating the values so obtained. Tables are given showing that the percentage of chlorine in the liquid chloride continuously diminishes until the value 57 per cent. is reached, which is slightly greater than that corresponding with the compound S_2Cl_2 ; during this interval, the vapour is always much richer in chlorine than the liquid, the percentage of that element in the vapour falling from 85.2 to 68.2 at -10° , whilst the percentage in the liquid changes from 70.1 to 57.9. The conclusion is drawn that the sulphur dichloride between -10° and 0° is a mixture of several substances, and is not a definite individual.

Additional information was obtained by observing the melting point of chlorinated products containing from 51.5 to 92.5 per cent. of chlorine. The curve illustrating the results shows two maxima at -80° and -30.5° , the composition of the liquid at these points corresponding with the compounds S_2Cl_2 and SCl_4 . There is also an indication of a maximum outside the curve practically realised, which corresponds with a compound SCl_{11} . The eutectic mixture melts at -113° , and its solidification, which occurs at -113° and causes a sudden rise of temperature to -101.3° , clearly shows it to be a mixture of sulphur monochloride and tetrachloride, and of

these two substances only. There is no evidence of the existence of the compound SCL_2 .
W. A. D.

Influence of Impurities on the Specific Gravity of Sulphuric Acid. ARTHUR MARSHALL (*J. Soc. Chem. Ind.*, 1902, 21, 1508—1511).—The addition of nitric acid (94.0 per cent. strength) to sulphuric acid (96.5 per cent., sp. gr. 1.8437 at $18^\circ/18^\circ$) increases the gravity of the latter, a maximum (1.862 at $18^\circ/18^\circ$) being reached with about 7.5 per cent. of nitric acid. Further addition then causes the gravity to diminish. Extremely small quantities of nitric acid are found to have a marked effect on the gravity. A table is given showing the increases in gravity of various strengths of sulphuric acid, caused by the addition of 0.1 per cent. of sodium, magnesium, calcium, aluminium, iron, and lead sulphates. In some cases, these salts were not soluble in the acid to the extent of 0.1 per cent. The author has recalculated Pickering's table of specific gravities (*Trans.*, 1890, 57, 152) into percentages of H_2SO_4 for each interval of 0.001 in the gravity.
W. P. S.

Certain Tellurium Minerals and the Action of Sulphur Monochloride on them. R. W. EMERSON MACIVOR (*Chem. News*, 1902, 86, 308).—Native tellurium, of sp. gr. 6.22, containing Te 96.94 and Au 2.4 per cent., and calaverite from Kalgoorlie, Western Australia, of sp. gr. 9.314, containing Te 57, Au 42.15, and Ag 0.60 per cent., were both completely decomposed by heating in the finely powdered condition with sulphur monochloride, tellurium tetrachloride being formed and sulphur liberated.
D. A. L.

Preparation of Nitrogen from Ammonium Nitrite. GEORG VON KNORRE (*Chem. Centr.*, 1903, i, 125; from *Chem. Ind.*, 1902, 25, 531—536).—The original paper contains a *résumé* of previous work on the preparation of nitrogen. Experiments have shown that the gas obtained from ammonium nitrate always contains nitric oxide. This gas may be removed by means of an acid solution of a ferrous salt or an acid solution of potassium permanganate, but in the former case the ferrous solution is liable to give up a portion of the dissolved nitric oxide when shaken with an indifferent gas, and in the latter, variable quantities of oxygen are liberated in the oxidation of the nitric oxide to nitric acid. Nitric oxide is best removed by treating the gas with a mixture of 5 vols. of a saturated solution of potassium dichromate and 1 vol. of concentrated sulphuric acid. The gas obtained by heating a solution of sodium nitrite and ammonium nitrate in 45 c.c. of water contained 1.3—1.9 per cent. of nitric oxide, and the addition of potassium dichromate to the mixture was found to increase the quantity of oxide. If the air is removed from the flask before heating, the nitric oxide is only formed towards the end of the reaction. When a large excess of ammonium chloride is used, the nitrogen contains only 0.9 per cent. of nitric oxide, and in the latter stages of the action it contains none. A mixture of 3 parts of ammonium sulphate to 1 of nitrite yields

a gas which does not contain a measurable quantity of nitric oxide. The presence of ammonia renders the action slower, but prevents the formation of nitric oxide, whilst addition of salts which react to form ammonia, such as potassium chromate, disodium hydrogen phosphate, or sodium tungstate, also renders the gas free from nitric oxide. The presence of the sulphates of iron, zinc, or copper, on the other hand, promotes the formation of nitric oxide.

Pure nitrogen is best prepared by heating a solution of 1 part of sodium nitrite with 1—2 of ammonium sulphate and 1 of potassium dichromate and washing the gas by passing it through a Lunge 10 bulb tube containing dilute sulphuric acid or a mixture of potassium dichromate and sulphuric acid as just described. E. W. W.

Burning of Nitrogen to Nitric Oxide in the Electric Flame. WILHELM MUTHMANN and HANS HOFFER (*Ber.*, 1903, 36, 438—453).—In the experiments described, the current was obtained from a 1·5 kilowatt alternating dynamo transformed from 25 amperes at 20 volts to 0·05—0·15 ampere at 2,000—4,000 volts. The temperature of the flame diminishes with an increase in the distance between the electrodes, but its height increases. The temperature was measured by the amount of dissociation caused by the current passing through carbon dioxide under the same conditions as in air. For a distance of 1 cm. between the electrodes with 8 amperes and 15 volts in the primary circuit, the temperature was 1825°, whilst for 1·5 and 3·5 cm. with 12 amperes and 15 volts, and with 20 amperes and 17 volts respectively, the temperatures were 1800° and 1590° respectively. Tables are given showing the equilibria between nitric oxide, nitrogen, and oxygen corresponding with different distances of the electrodes, obtained by the flame passing through air and through nitric oxide; the proportion of nitric oxide is in all cases greatest when the flame is smallest and at the highest temperature, that is, when the electrodes are closest; thus in the case of air for the distances 0·4, 1·0, and 1·5 cm., the percentages of nitric oxide are 6·7, 4·3, and 3·7 respectively, and, starting with nitric oxide, 5·0, 4·5, and 4·6.

From a lengthy theoretical discussion on the economy of the process, the author considers that it should be possible to manufacture nitric acid electrically at about one-quarter the cost incurred in preparing it from Chili saltpetre, and that owing to the large amount of energy consumed in heating the excess of nitrogen, the efficiency of the method would be much enhanced by working with a mixture of oxygen and nitrogen in equal proportions and not with ordinary air.

W. A. D.

The Emanation of Phosphorus. EUGÈNE BLOCH (*Compt. rend.*, 1902, 135, 1324—1326).—A current of dry air was passed at a constant rate over dry phosphorus, and the conductivity of the air due to ionisation was determined. From the results so obtained, the author calculates the speed of the ions, which is about the same for both kinds, to be 1/300 mm. per second for a fall of potential of 1 volt per cm. The nature of the emanation is unknown; it is considerably weakened in its effects by passing the air through glass wool or

through certain solutions. The ions present an analogy with those obtained by Townsend (*Phil. Mag.*, 1898, 45, 125) by the electrolytic process. The ions also act as nuclei for cloud production, even in gases not quite saturated with moisture. J. McC.

Phosphorus Suboxide and the Supposed Solubility of Red Phosphorus in Aqueous Alcoholic Alkalis. AUGUST MICHAELIS and K. VON AREND (*Annalen*, 1902, 325, 361—367. Compare Abstr., 1900, ii, 137; and 1901, ii, 153).—It is pointed out that the analyses of the supposed suboxide carried out by Burgess and Chapman (*Trans.*, 1901, 79, 1235) to show that this substance was merely impure red phosphorus are in reality very good evidence for the existence of the suboxide; the mean of their results gives 88.51 per cent. of phosphorus, whereas phosphorus suboxide requires 88.57 per cent. The solubility of red phosphorus in aqueous alcoholic alkalis (Burgess and Chapman, *loc. cit.*) is not confirmed. Pure red phosphorus, whether commercial or prepared by heating phosphorous acid and phosphorus trichloride, is insoluble in this medium; when red phosphorus is rubbed with water for a long time, it is to a small extent oxidised, yielding the suboxide and acids of phosphorus; at the same time, a small amount of ordinary phosphorus is formed, which dissolves when the mixture is treated with alkaline solutions. K. J. P. O.

Action of Ammonia on Phosphorus Pentasulphide and the Nitride of Phosphorus, P_3N_5 . ALFRED STOCK and BERTHOLD HOFFMANN (*Ber.*, 1903, 36, 314—319).—At the ordinary temperature, phosphorus pentasulphide and ammonia form a yellow *additive* product, $P_2S_5 \cdot 6NH_3$, whilst at -20° a colourless *additive* product, $P_2S_5 \cdot 7NH_2$, is obtained. When the yellow additive product, or phosphorus pentasulphide, is dissolved in liquid ammonia, a reaction occurs in which two substances are formed, one of which is insoluble in liquid ammonia and crystallises out, whilst the other is obtained by evaporating the ammonia; the former is *ammonium iminotri thiophosphate*, $(NH_4S)_3P:NH$, the latter compound is *ammonium nitrilodithiophosphate*, $(NH_4S)_2P:N$. These reactions of the additive products of phosphorus pentasulphide and ammonia show that the latter are probably ammonium salts of thiophosphates; thus, $P_2S_5 \cdot 6NH_3$, is ammonium di-iminopentathiopyrophosphate, $[(NH_4S)_2P:NH]_2S$.

When either of the additive products of phosphorus pentasulphide and ammonia or the thiophosphates just mentioned are heated, or when phosphorus pentasulphide is slowly heated in gaseous ammonia up to 230° , *phosphorus nitride*, P_3N_5 , is produced; it is a colourless, odourless, tasteless, and completely insoluble substance which can be heated to redness, only decomposing into phosphorus and nitrogen at a bright red heat; when heated in hydrogen, ammonia is produced; boiling water decomposes it very slowly into ammonia and phosphoric acid, but the decomposition takes place rapidly and quantitatively at 180° ; when heated with chlorine or oxygen, the nitride takes fire; with many metals, phosphides are formed; some metallic oxides, such as lead oxide and arsenic oxide, are reduced.

It is possible that Briegleb and Geuther (*Annalen*, 1862, 123, 235)

obtained phosphorus nitride mixed with magnesium chloride by heating magnesium nitride with phosphoric chloride; whether the so-called phosphamide contains phosphorus nitride seems doubtful (compare Besson, *Abstr.*, 1892, 1152).

Attention is drawn to the fact that the compound of phosphorus and nitrogen is stable, just as are the compounds of aluminium and boron, carbon and silicon, and of sulphur and oxygen. K. J. P. O.

Arsenic Pentachloride. CHARLES BASKERVILLE and H. H. BENNETT (*J. Amer. Chem. Soc.*, 1902, 24, 1070—1072).—To prepare the pentachloride, about 5 c.c. of purified arsenic trichloride, in a dry test-tube cooled by solid carbon dioxide loosely packed in a Dewar bulb, are saturated with chlorine. The crystalline trichloride (m. p. -18°) assumes a greenish-yellow colour and becomes liquid. After distilling off the excess of chlorine at -31° , the residual liquid has the composition AsCl_5 . *Arsenic pentachloride* is readily soluble in carbon disulphide and ether at -30° , and either crystallises from these solvents, or solidifies alone at about -40° in yellow prisms. When heated above -25° , it begins to decompose, and on exposure to the air it evolves fumes of hydrogen chloride. E. F. A.

Action of Ammonia on Boron Sulphide. ALFRED STOCK and MARTIN BLIX (*Ber.*, 1903, 36, 319—320. Compare this vol., ii, 207).—Although the compounds of boron chloride, bromide, and iodide with ammonia are probably mixtures of bor-amide or -imide with ammonium chloride, &c., as Joannis (this vol., ii, 140) has suggested, it is thought that the analogous compound of boron sulphide and ammonia is really an additive product, $\text{B}_2\text{S}_3 \cdot 6\text{NH}_3$ (compare *Abstr.*, 1901, ii, 650); this does not lose ammonium sulphide by volatilisation at the ordinary temperature, and it dissolves completely in liquid ammonia, and does not leave a residue of the insoluble borimide.

K. J. P. O.

Sodium Salt of Percarbonic Acid. SIMEON M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 952—954. Compare *Abstr.*, 1901, ii, 482).—The author gives the results of investigations on the distribution of hydrogen peroxide between water or aqueous solutions of sodium carbonate on the one hand and ether on the other. It is found that sodium carbonate in aqueous solution combines with a part of the hydrogen peroxide. Hence the sodium salt of percarbonic acid does not undergo complete hydrolysis, the degree of the latter increasing as the temperature is raised or the concentration diminished. No definite conclusions as to the rôle of the hydrogen peroxide can be drawn from these observations. T. H. P.

New Preparation of Liquid Silicon Hydride, Si_2H_6 . HENRI MOISSAN (*Compt. rend.*, 1902, 135, 1284. Compare *Abstr.*, 1902, 318, 560).—When lithium silicide, Si_2Li_6 , is gently heated in a

current of dry hydrogen chloride, hydrogen is evolved and a residue of lithium chloride and silicon chloride is obtained. A dilute solution of hydrochloric acid decomposes lithium silicide with evolution of pure hydrogen, but with concentrated hydrochloric acid silicon hexahydride, Si_2H_6 , is produced, and can be condensed by passing the gas into a receiver cooled to -200° by means of liquid air. J. McC.

Presence of Argon in the Gas of the Bordeu Spring at Luchon and the Presence of Free Sulphur in the Sulphur-waters of the Grotto and in the Vapours used for Inhalation. HENRI MOISSAN (*Compt. rend.*, 1902, 135, 1278—1283).—The temperature of the water of the Bordeu Spring at Luchon is about 44° at the exit. The water slowly evolves gas, which consists of 1.22 per cent. of methane, 2.56 per cent. of argon, and 96.22 per cent. of nitrogen; it does not contain carbon dioxide, oxygen, helium, and hydrogen sulphide. The hydrogen sulphide present in the air at the well is consequently a secondary product formed by the action of the carbon dioxide of the air on the dissolved sodium sulphide.

The water of the Grotto at Luchon contains some free sulphur in solution, and the vapour evolved from this water contains traces of hydrogen sulphide and of sulphur dioxide as well as some free sulphur. The free sulphur has three sources: (1) vaporisation of sulphur from the water, (2) slow combustion of the hydrogen sulphide, and (3) the interaction of the hydrogen sulphide and the sulphur dioxide. The presence of the free sulphur is of great therapeutic value. J. McC.

Action of Iodine on Alkalis. FRITZ FOERSTER and K. GYR (*Zeit. Elektrochem.*, 1903, 9, 1—10).—When solutions of iodine and an alkali hydroxide are mixed, hypoiodous acid and a hypoiodite are formed, but the reactions are not complete; the final solution contains free iodine and alkali, together with hypoiodous acid and hypoiodite; $\text{I}_2 + \text{OH}' \rightleftharpoons \text{HOI} + \text{I}'$, and $\text{HOI} + \text{OH}' \rightleftharpoons \text{IO}' + \text{H}_2\text{O}$. That the first reaction is reversible may be shown by adding hypoiodous acid to a solution of potassium iodide, or by adding potassium iodide to a dilute solution of iodine in an alkali hydroxide; free iodine is liberated in either case. Since hypoiodous acid is a very weak acid, its salts are hydrolysed to a very considerable extent in aqueous solution. According to the equations just given, diminution of the hydroxyl concentration of an alkaline iodine solution increases the amount of free iodine present; this explains the effect of an addition of a hydrogen carbonate or an acid to such a solution. Solutions of hypoiodites are very unstable; if equal volumes of 0.1 *N*-iodine and *N*-sodium hydroxide solutions are mixed, the resulting solution contains about 95 per cent. of the theoretical quantity of hypoiodite immediately after mixing, but 2 minutes later only 75 per cent. The change which takes place appears to be analogous to the formation of chlorate, $\text{KOI} + 2\text{HOI} = \text{KIO}_3 + 2\text{HI}$. This equation explains also the relative stability of solutions of pure hypoiodous acid. Excess of alkali, by diminishing the concentration of the hypoiodous acid, diminishes the velocity of the iodate formation, excess of iodide increases it.

The action of neutral oxidising agents on a solution of potassium iodide liberates iodine and potassium hydroxide, and therefore leads to the formation of the products of their interaction. The action of oxygen, ozone, hydrogen peroxide, and potassium periodate on potassium iodide is discussed.

T. E.

The so-called Electrolytic Reduction of Potassium Chlorate. ANDRÉ BROCHET (*Compt. rend.*, 1903, 136, 155—157).—When a solution of potassium chlorate is electrolysed with a copper anode, the brown precipitate formed is not pure copper oxide. The copper oxide is formed by an abnormal reaction, $\text{Cu}(\text{ClO}_3)_2 + 6\text{Cu} = \text{CuCl}_2 + 6\text{CuO}$, the normal reaction when an alkali salt is electrolysed with a soluble anode being the formation of a salt of the metal, which is then precipitated by the alkali formed at the cathode. This direct action of copper on copper chlorate can be shown by warming a concentrated solution of copper chlorate with copper; after boiling for an hour, silver nitrate precipitates silver chloride from the solution. The copper oxide precipitated contains some metallic copper and a small quantity of cuprous chloride. It is proved that the yield of chloride by electrolysis is too great to be accounted for by the reaction $\text{KClO}_3 + 3\text{H}_2 = \text{KCl} + 3\text{H}_2\text{O}$, and in contradistinction to the views of Bancroft (*Trans. Amer. Electrochem. Soc.*, 1, 65) and of Burrows (this vol., ii, 7) the author believes that potassium chlorate is not directly reducible, and that its supposed reduction is due to the intermediary reaction of the copper on the copper chlorate.

J. McC.

Electrolytic Preparation of Sodium Amalgam. E. S. SHEPHERD (*J. Physical Chem.*, 1903, 7, 29—30).—The electrolytic preparation of sodium amalgam makes a convenient lecture experiment if the mercury cathode be contained in a porous pot dipping into the electrolyte, which may be a saturated solution of sodium chloride. The mercury, if desired, may be coated with molten naphthalene, and at a temperature of 90° an efficiency as high as 60 per cent. may be attained, the voltage required being only about 6 volts.

L. M. J.

Solubility of Silver Chloride in presence of Mercuric Salts. BICE FINZI (*Gazzetta*, 1902, 32, ii, 324—329).—When solutions containing equivalent proportions of mercuric chloride and silver nitrate are mixed, less than the quantitative amount of silver chloride is precipitated, the dissolved portion increasing with the amount of water present; the filtrate from the precipitated silver chloride gives a precipitate with hydrochloric acid, chlorides, silver nitrate, ammonium nitrate, sulphate, acetate, or citrate. The silver chloride, in all probability, exists in the solution in a dissociated state brought about by the presence of the mercuric nitrate. The presence of an alkali acetate does not facilitate the precipitation of the silver chloride, and when the proportion of acetate is equivalent to that of the mercuric chloride, the silver chloride retained in solution is increased in quantity. By augmenting the amount of mercuric chloride present, the quantity of precipitated silver chloride is increased.

T. H. P.

[Electrolytic] Preparation of Calcium. WILHELM BORCHERS and LORENZ STOCKEM (*Ber.*, 1903, 36, 17—18).—Ruff and Plato's method of preparing calcium (this vol., ii, 19) has no advantage over the older method of Bunsen and Matthiessen, and has the disadvantage that the fused calcium separating at the cathode partly dissolves in the fused calcium chloride to form the crystalline subchloride, CaCl .

W. A. D.

Preparation of Calcium. OTTO RUFF and WILHELM PLATO (*Ber.*, 1903, 36, 491. Compare this vol., ii, 76, 145).—The process described by Borchers and Stockem is stated to be practically identical with one previously patented by the authors.

J. J. S.

Solubility of Gypsum in Presence of Metallic Chlorides. N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 949—951).—The amounts of calcium sulphate dissolved by 1000 parts of water containing 1 and 40 per cent. of calcium chloride are 1.1414 and 0.2130 respectively; for water to which 1 and 20 per cent. of sodium chloride are added, the corresponding numbers are 3.3992 and 7.3739 respectively. Tables are given showing the solubilities of calcium sulphate in solutions containing quantities of calcium or sodium chloride between the above limits.

T. H. P.

Periodates of Lead and Copper. F. GIOLITTI (*Gazzetta*, 1902, 32, ii, 340—354).—The lead periodate which is obtained by adding a solution of lead acetate acidified with acetic acid to a cold solution of dipotassium hydrogen periodate (K_2HIO_5), to which several investigators have assigned the formula $\text{Pb}_3\text{I}_2\text{O}_{10} \cdot 2\text{H}_2\text{O}$, is shown by the author to have the composition PbHIO_5 ; when heated, it yields the salt $\text{Pb}_2\text{I}_2\text{O}_9$. Lead periodates having the following formulæ have also been prepared: $\text{PbHIO}_5 \cdot \text{H}_2\text{O}$; Pb_2HIO_6 ; $\text{Pb}_3\text{I}_2\text{O}_{10} \cdot \text{H}_2\text{O}$; and $\text{Pb}_3\text{I}_2\text{O}_{10}$.

New copper periodates have been prepared having the compositions: Cu_2HIO_6 ; $\text{Cu}_4\text{I}_2\text{O}_{11}$; $\text{Cu}(\text{IO}_4)_2$; $\text{Cu}_5\text{I}_2\text{O}_{12} \cdot 7\text{H}_2\text{O}$; and $\text{Cu}_5\text{I}_2\text{O}_{12} \cdot 3\text{H}_2\text{O}$.

The behaviour of these copper periodates tends to confirm Rosenheim and Liebknecht's view (*Abstr.*, 1899, ii, 743), derived from the stability and ease of formation of penta-argentic periodate, that the normal form of periodic acid is the pentabasic one. On the other hand, the fact that lead, in spite of its marked tendency to yield basic salts, gives nothing beyond triplumbic periodate, indicates that periodic acid is tribasic.

T. H. P.

Salts and Double-salts of Tervalent Thallium. RICHARD J. MEYER and E. GOLDSCHMIDT (*Ber.*, 1903, 36, 238—244).—When dilute sulphuric acid is saturated at the boiling temperature with thallic oxide, an acid solution is obtained which, on cooling, deposits crystals of the formula $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, whilst at a lower temperature crystals of the composition $\text{HTl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ are obtained. Attempts to prepare a potash-alum gave only the salt $\text{KTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$;

ammonium and rubidium sulphates gave the salts $\text{AmTl}(\text{SO}_4)_2$ and $\text{CsTl}(\text{SO}_4)_2$, either anhydrous or with $4\text{H}_2\text{O}$, whilst lithium and sodium gave the salts $\text{LiTl}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ and $\text{NaTl}(\text{SO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. Thallous sulphate and bromine gave the bromosulphate, $\text{Tl}_2\text{Br}_2\text{SO}_4$, probably $\text{Tl}'\text{O} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{Tl}'''\text{Br}_2$.

Thallic acetate, $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)_3$, crystallises in anhydrous, glistening flakes from a solution of thallic oxide in acetic acid saturated at the boiling temperature; it is decomposed by moisture, but the ammonium acetate, $\text{NH}_4\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)_4$, crystallises in glistening prisms and is stable in the air.

Thallic hydrogen oxalate, $\text{HTl}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, is prepared by precipitating a solution of moist thallic oxide in acetic acid by means of oxalic acid.

T. M. L.

Alloys of Mercury. N. N. PUSHIN (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 856—904).—The author has made determinations of the melting points of amalgams of varying composition of zinc, cadmium, bismuth, lead, and tin, and of the *E.M.F.* of certain galvanic elements containing, as one of the electrodes, an amalgam of one of the above metals or of copper. The results are given in both curves and tables. Microphotographic representations of the structures of some of the amalgams are also given.

T. H. P.

Cerium and Lanthanum. WILHELM MUTHMANN and K. KRAFT (*Annalen*, 1902, 325, 261—278. Compare Abstr., 1902, ii, 262).—The preparation of cerium by electrolysis of the chloride (*loc. cit.*) has been considerably improved; the chloride is mixed with barium chloride, which is added slowly during the electrolysis, a current of 100 amperes and 10—15 volts being used. Lanthanum can be prepared in a similar manner, but not in such good yield, from the very hygroscopic lanthanum chloride.

Cerium hydride, which Winkler first obtained mixed with magnesia (Abstr., 1891, ii, 801), is prepared by passing pure hydrogen over turnings of cerium heated at $250\text{--}270^\circ$; the metal burns with a brilliant flame in the gas; the mean of a number of not very concordant analyses gives 2.4 per cent. as the amount of hydrogen present, which agrees most nearly with the formula CeH_3 . The hydride is a brittle, reddish-brown or black solid; it is stable in dry air, but rapidly decomposes in moist air, often catching fire; when heated in dry air, hydrogen is evolved and a mixture of cerium dioxide and nitride left; it dissolves in acids with the evolution of hydrogen and the formation of cerous salts.

Lanthanum hydride, LaH_3 , resembles cerium hydride closely, but is more stable in the air; the reaction between lanthanum and hydrogen begins at 240° , the lanthanum burning in the hydrogen with a reddish-yellow light. When heated in the air, lanthanum nitride is largely formed.

Cerium nitride, CeN , is easily prepared by passing perfectly pure nitrogen (obtained by passing the gas from sodium nitrite and ammon-

ium chloride over red hot copper and iron wire) over red hot cerium (at 850°), when the cerium burns in the nitrogen with a brilliant, white light. The nitride is lustrous and brass yellow to bronze in colour, and is stable in dry air, but in moist air is converted into cerium dioxide with evolution of ammonia; when moistened with a few drops of water, a violent reaction sets in, the substance being heated to redness; it decomposes slowly when treated with alkalis, cerous hydroxide and ammonia being formed; with acids, cerous and ammonium salts are produced. On heating the hydride in nitrogen, or cerium in ammonia, a black, pyrophoric substance is formed.

Lanthanum nitride, LaN , is formed by absorption of the gas by the metal at a red heat; this metal does not burn in nitrogen; the nitride is a dull black solid which slowly decomposes in moist air with evolution of ammonia; it is also formed when lanthanum is heated in dry ammonia. When lanthanum is burnt in dry air, more than half the metal is converted into nitride; the union of lanthanum with nitrogen begins at a lower temperature than with oxygen.

Both cerium and lanthanum reduce carbon monoxide and dioxide; with methyl chloride, cerium reacts at $500\text{--}600^{\circ}$, giving a mixture of chloride, hydride, and carbon. Both ethylene and acetylene react with lanthanum, yielding the hydride and carbon.

The temperature of ignition of cerium in oxygen is $150\text{--}180^{\circ}$, and that of lanthanum $440\text{--}460^{\circ}$; under similar conditions, magnesium ignites at 540° and aluminium at 580° . K. J. P. O.

Specific Heat of some Cerium and Lanthanum Compounds.

F. KELLENBERGER and K. KRAFT (*Annalen*, 1902, 325, 279—281).—The specific heat of cerium hydride is 0.088915; the mol. heat amounts to 12.715, whence the atomic heat of hydrogen is 2.15 if that of cerium is taken as 6.27, Hillebrandt's value (this *Journal*, 1877, i, 50). The specific heat of lanthanum hydride is 0.087335, and the mol. heat 12.314; if the atomic heat of the metal be taken as 6.189 (Hillebrandt's value) the atomic heat of hydrogen is 2.06. Kopp's mean value for the atomic heat of hydrogen is 2.3. The mol. heat of cerium nitride is 11.14, whence the atomic heat of nitrogen is 4.87. The specific heat of lanthanum nitride is 0.07265, the mol. heat 11.043, which gives the value 4.85 for the atomic heat of nitrogen. These values for the atomic heat of nitrogen lie close to the value 5, now generally accepted, but do not agree with Kopp and Neumann's number, 6.3. K. J. P. O.

Dissociation of Lanthanum Hydride and Cerium Hydride.

WILHELM MUTHMANN and E. BAUR (*Annalen*, 1902, 325, 281—291).—A series of experiments has been made to determine the dissociation pressure of lanthanum hydride at various temperatures. A specially constructed apparatus of a very simple kind was used, in which the temperature was measured by a platinum-platinum-rhodium junction. At a given temperature, equilibrium was very soon attained, but the

pressure, however, did not remain constant, but slowly changed if the heating was continued. Other experiments, made with different specimens of the hydride, gave the most paradoxical results; in some cases, at a given temperature, a definite, although small, dissociation pressure developed, to be followed by a recombination without alteration of the conditions; other specimens under the same conditions did not show this behaviour. Cerium hydride behaved in much the same manner. It is suggested that these hydrides undergo a slow, peculiar change of their molecular structure, which would be accompanied by a change in the dissociation pressure. Such an observation is unique and at present without analogy.

K. J. P. O.

Indirect Oxidation by Salts of the Rare Earths. ANDRÉ JOB (*Compt. rend.*, 1903, 136, 45—47. Compare Abstr., 1902, i, 431).—Cerous acetate, when added to a solution of quinol, brings about the oxidation of the latter even more rapidly than manganous acetate, although the cerous salt itself is not readily oxidised by air. The effect is probably due to the intermediate formation of cerium peroxide, the existence of which is known. Lanthanum acetate is as active as cerous acetate in causing the oxidation of quinol, and this fact indicates very cogently the existence of a lanthanum peroxide, which, however, is not necessarily identical with the unstable peroxide precipitated from solutions of lanthanum salts by ammonia and hydrogen peroxide.

C. H. B.

Cryolites. E. BAUD (*Compt. rend.*, 1902, 135, 1337—1339).—When a solution of sodium fluoride is added to a solution of aluminium fluoride, a gelatinous precipitate of the salt, $2\text{AlF}_3 \cdot 6\text{NaF} \cdot 7\text{H}_2\text{O}$, is obtained. One hundred c.c. of water at 16° dissolve 0.352 gram of this hydrate, and the heat of solution is -25.87 Cal. The heat of formation from soluble solid aluminium fluoride, $2\text{AlF}_3 \cdot 7\text{H}_2\text{O}$, and solid sodium fluoride is $+19.29$ Cal. A similar reaction takes place with potassium fluoride; the gelatinous precipitate has the composition $2\text{AlF}_3 \cdot 6\text{KF} \cdot 7\text{H}_2\text{O}$, and is soluble to the extent of 0.385 gram in 100 c.c. of water at 16° . The heat of solution is -40.64 Cal. at 16° , and the heat of formation (as for the sodium compound) is $+55.89$ Cal. When a solution of 6 mols. of ammonium fluoride is added to a solution of one molecule of aluminium fluoride, a double fluoride, $2\text{AlF}_3 \cdot 4\text{NH}_4\text{F} \cdot 3\text{H}_2\text{O}$, is formed. When the solutions are mixed, the temperature rises for 2 minutes, then remains stationary for 2 to 3 minutes, and for the following 15 minutes again rises. The precipitate is at first gelatinous, but becomes denser and settles well; the polymerisation is accompanied by a development of 3.7 Cal. About one gram of the double salt is soluble in 100 c.c. of water at 16° . The heat of solution at 16° is -17.09 Cal. Natural sodium cryolite is almost anhydrous; 100 c.c. of water at 15° dissolve 0.034 gram of it. The heat of hydration was found from the heats of solution of natural cryolite, dehydrated cryolite, and hydrated cryolite in 19 per cent. hydrofluoric acid. For the first two, practically the same heat, $+58.52$ Cal., was found, whilst for the

hydrated cryolite + 13.98 Cal. was obtained. The difference, 44.54 Cal., represents the heat of hydration ($7\text{H}_2\text{O}$) of $2\text{AlF}_3, 6\text{NaF}$. From these data, the author calculates:



The heat of hydration of anhydrous potassium cryolite has been found to be +33.04 Cal., and its heat of formation from 2AlF_3 and 6NaF is +87.80 Cal.

It is evident, therefore, that the potassium salt is more stable than the sodium derivative, just as has been found for the corresponding compounds of the type $2\text{AlCl}_3, 6\text{MCl}$. J. McC.

Two Silicides of Manganese. PAUL LEBEAU (*Compt. rend.*, 1903, 136, 89—92).—A manganese silicide, Mn_2Si , was prepared by Vigouroux (Abstr., 1896, ii, 362), and more recently another silicide, MnSi_2 , was obtained by De Chalmot (Abstr., 1896, ii, 560) by heating a mixture of quartz, manganese dioxide, lime, and carbon. Carnot and Goutal (*Ann. des Mines*, 1900, [ix], 18, 271) have also demonstrated the presence of a silicide, MnSi (?), in the residue left after the action of sulphuric acid on ordinary castings. The silicide, Mn_2Si , was prepared by a method similar to that previously used in the preparation of iron and cobalt silicides (Abstr., 1902, ii, 135, 264, 457, and this vol., ii, 22, 80), an alloy of copper and manganese being mixed with crystalline silicon and fused for two minutes in the electric furnace; the metallic ingot thus formed is treated with nitric acid and the residue extracted with 10 per cent. sodium hydroxide; this silicide can also be prepared by heating in a crucible in an electric furnace a mixture of sodium, potassium silicofluoride, the manganese oxide, Mn_3O_4 , and copper; the silicide forms very lustrous, apparently quadratic prisms of sp. gr. 6.20 at 15° ; it scratches glass, but is cut by quartz. Both concentrated and dilute hydrochloric acid dissolve the compound readily, but nitric acid is without action; alkali hydroxides slowly destroy it, gelatinous silica being formed.

The silicide, MnSi , is prepared in the same manner as the compound just described, only a larger proportion of silicon being used; it forms highly lustrous, tetrahedral crystals having the density 5.9 at 15° ; it is harder than the other silicide, scratching topaz, but not corundum; this silicide differs from the former in that hydrochloric acid attacks it very slowly; both nitric and sulphuric acids are without action; the halogens and the gaseous halogen hydrides attack it easily.

K. J. P. O.

Colouring Matter of the Figure in the Grotto at La Mouthe. HENRI MOISSAN (*Compt. rend.*, 1903, 136, 144—146).—The pigment of the design on the wall of the grotto at La Mouthe is black on account of the presence of manganese oxide. Some objects found in the grotto are covered with a black deposit of manganese dioxide.

J. McC.

Manganese Borate. H. ENDEMANN and JOHN W. PAISLEY (*Amer. Chem. J.*, 1903, 29, 68—73).—Commercial manganese borate is a

mixture of varying composition. The precipitates obtained by the action of borax on manganous chloride or sulphate lose boric acid on washing. A definite product may be obtained by adding to such moist precipitates the quantity of boric acid required to form a substance of the composition $\text{MnO}, \text{B}_4\text{O}_6$, and then allowing them to dry spontaneously. When this mixture is heated with a little water in a sealed tube, the compound, $\text{MnB}_4\text{O}_7, 5\text{H}_2\text{O}$, is obtained as a granular mass; when heated to 120° , it loses $2\text{H}_2\text{O}$, but readily reabsorbs water and sets to a hard mass. Both the hydrated salts readily yield their manganese to hot oils, producing quick-drying varnishes. E. G.

[Reactions of] Cobalt and Nickel. JULIUS MAI and M. SILBERBERG (*Chem. Zeit.*, 1903, 27, 13—14).—Contrary to expectation, moist nickel peroxide is instantly soluble in a cold dilute solution of potassium cyanide, whilst the corresponding cobalt compound is scarcely affected. If, however, both oxides are present, it is not possible to extract all the nickel which is, probably, mechanically retained by the cobalt; on applying heat or using a concentrated solution of cyanide, the cobalt compound is also gradually dissolved.

Cobalt peroxide is also more stable than nickel peroxide towards such reagents as thiocyanates, hydroxylamine, &c. On adding sulphur dioxide to a solution of potassium cobaltcyanide, the colour changes to a red dichromate colour. This reaction is, in fact, due to the cobaltcyanide and not to the cobaltcyanide. The experiment succeeds best on adding sodium hydrogen sulphite to a freshly prepared solution of potassium cobaltcyanide; this solution yields, with most metallic salts, yellow or orange precipitates. If a solution of cobaltous sulphite is mixed with potassium cyanide, an orange-coloured salt of cobalt is precipitated which needs further analysis. L. DE K.

Salts of Uranium. WILLIAM ECHSNER DE CONINCK (*Ann. Chim. Phys.*, 1903, [vii], 28, 5—15).—This paper is a summary of the results of work previously published (Abstr., 1901, ii, 390, 536; and 1902, ii, 84, 458, and 664). K. J. P. O.

Tin Amalgams. H. W. BAKHUIS ROOZEBOOM [with VAN HETEREN] (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 373—376).—Liquid tin and mercury are miscible in all proportions, and the temperature at which solidification sets in has been determined for various mixtures; the results are represented graphically. The solid phase which separates at 25° contains 94 atomic per cent. of tin. The *E.M.F.* of tin amalgams containing from 0.001 to 100 atomic per cent. of tin was measured against an amalgam containing 16 atomic per cent. As the amount of tin increases up to 1.2 atomic per cent., the *E.M.F.* rises, but from this concentration up to 99 per cent. the potential remains constant; consequently, between these limits there must be two phases of constant concentration; one of these is a liquid with 1.2 atomic per cent. of tin, and the other is a solid

phase with 99 atomic per cent. of tin. The heat of amalgamation was found by comparing the *E.M.F.* of amalgams which are liquid at 25° and 50° respectively. The introduction of one gram-atom of tin into a liquid amalgam containing up to 1 atomic per cent. of tin absorbs 3000 cal.

On cooling the amalgams containing 0.3 to 85 per cent. of tin to -34.5° , a change takes place which is accompanied by a development of heat and a diminution of volume. The maximum change occurs when the amalgam contains about 50 per cent. of tin. All amalgams containing up to 60 per cent. of tin solidify finally at -38.6° . Between -34.5° and -38.5° , mixed crystals separate and expansion takes place. It has not been found possible to determine what modification of tin is then deposited, but its specific volume must be smaller than that of grey tin and larger than that of the ordinary variety. J. McC.

Reduction of Titanic, Vanadic, Tungstic, and Molybdic Acids by means of Nascent Hydrogen in Molecular and Quantitative Proportions. C. REICHARD (*Chem. Zeit.*, 1903, 27, 1—5).—When insoluble titanium dioxide is added to a mixture of zinc and dilute hydrochloric or sulphuric acid, from which the evolution of hydrogen is just appreciable, a pale lilac or very light blue coloration is seen; with alkali titanates, a pale violet coloration, which rapidly passes into dark blue, is obtained. Under the same conditions, molybdenum trioxide gives a brown coloration, soon becoming pale green. Molybdates give a transient, reddish-brown coloration and then a greyish-brown precipitate. Tungsten trioxide and tungstates give a pale blue coloration which gradually becomes darker. Solutions of vanadic acid, which are sulphur-yellow, are only reduced in the presence of a larger quantity of acid, and give first a pale bluish-green, then a pale green, and finally a dark green coloration. When the evolution of hydrogen is very feeble, a bluish coloration is first observed, which then passes through violet into green, a green precipitate finally being formed. Vanadates in concentrations above 1 per cent. give at first a violet, then a pale blue, and finally a greyish-blue coloration. A process is described by means of which the four elements may be separated from a mixture and detected.

K. J. P. O.

Titanium Sesquioxide and its Salts as Reducing Agents. EDMUND KNECHT (*Ber.*, 1903, 36, 166—169).—A solution of titanium trichloride, which in a concentrated form is now a commercial product, and can also be readily prepared by reducing a titanate salt (titanium tetrachloride or sulphate) by zinc dust in the presence of hydrochloric acid, is a most powerful reducing agent. It reduces sodium sulphite to sulphide, and in alkaline solution to hyposulphite; cupric salts are reduced to cuprous salts and then to metallic copper; ferric salts are reduced in the cold, immediately and quantitatively. Nitric acid and nitrates are converted into ammonia. Organic nitro-compounds are easily reduced; titanium trichloride forms a most

convenient agent for the partial reduction of polynitro-derivatives. Azo-compounds are immediately reduced. Unsaturated aliphatic compounds such as fumaric acid are slowly reduced.

Titaniumsesquioxide or its hydrate, prepared by precipitating titanium trichloride by sodium hydroxide, can be used as a powerful solid reducing agent.

K. J. P. O.

Halogen Double-salts of Pentavalent Antimony and their Parent Acids. RUDOLPH F. WEINLAND and C. FEIGE (*Ber.*, 1903, 36, 244—260).—*Potassium meta-antimonichloride*, $\text{KSbCl}_6 \cdot \text{H}_2\text{O}$, crystallises in greenish-yellow, six-sided, hexagonal plates belonging to the rhombic system [$a : b : c = 0.8889 : 1 : 0.7794$], absorbs moisture from the air, but effloresces over sulphuric acid or calcium chloride. The *ammonium* salt, $\text{NH}_4\text{SbCl}_6 \cdot \text{H}_2\text{O}$, is isomorphous with the potassium salt [$a : b : c = 0.8909 : 1 : 0.7846$]. The *rubidium* salt, RbSbCl_6 , is anhydrous and forms thin, six-sided, yellowish-green, rhombic tablets [$a : b : c = 0.6719 : 1 : 0.8136$]. The *lithium* salt, $\text{LiSbCl}_6 \cdot 4\text{H}_2\text{O}$, forms square, hygroscopic tablets. The *glucinum* salt, $\text{Be}(\text{SbCl}_6)_2 \cdot 10\text{H}_2\text{O}$, forms small, yellowish, hygroscopic needles. The *calcium* salt, $\text{Ca}(\text{SbCl}_6)_2 \cdot 9\text{H}_2\text{O}$, forms long, hygroscopic needles. The *aluminium* salt, $\text{Al}(\text{SbCl}_6)_3 \cdot 15\text{H}_2\text{O}$, forms greenish-yellow, hygroscopic needles. The *chromium* salt, $\text{Cr}(\text{SbCl}_6)_3 \cdot 13\text{H}_2\text{O}$, forms grey-violet, flat, hygroscopic needles. *Magnesium pyroantimonichloride*, $\text{MgSbCl}_7 \cdot 9\text{H}_2\text{O}$, forms greenish-yellow, hygroscopic, triclinic tablets [$a : b : c = 0.7144 : 1 : 2.595$; $\alpha = 100^\circ 22'$, $\beta = 88^\circ 3'$, $\gamma = 91^\circ 16'$]. *Chromium orthoantimonichloride*, $\text{CrSbCl}_8 \cdot 10\text{H}_2\text{O}$, forms grey, hygroscopic plates. The *ferric* salt, $\text{FeSbCl}_8 \cdot 8\text{H}_2\text{O}$, forms yellow, hygroscopic, four-sided, tetragonal tablets [$a : c = 1 : 1.0112$].

Hydrogen meta-antimonibromide, $\text{HSbBr}_6 \cdot 3\text{H}_2\text{O}$, crystallises from a solution containing antimony tribromide, bromine, and hydrobromic or sulphuric acid in hygroscopic, irregular, six-sided, black tablets, which readily lose bromine and leave antimony tribromide. The *potassium* salt, $\text{KSbBr}_6 \cdot \text{H}_2\text{O}$, forms stout, six-sided, black tablets and readily loses bromine in the air. The *ammonium* salt resembles the potassium salt. The *lithium* salt, $\text{LiSbBr}_6 \cdot 4\text{H}_2\text{O}$, forms black, square, hygroscopic tablets. The *ferric* salt, $\text{Fe}(\text{SbBr}_6)_3 \cdot 14\text{H}_2\text{O}$, forms black, irregular, six-sided tablets and is very hygroscopic. The *nickel* salt, $\text{Ni}(\text{SbBr}_6)_2 \cdot 12\text{H}_2\text{O}$, forms beautiful, black, glistening, irregular, six-sided tablets.

The *cæsium* salt, $2\text{SbBr}_5 \cdot 3\text{CsBr} \cdot 2\text{H}_2\text{O}$, forms a black, microcrystalline powder and loses bromine in the air. The *glucinum* salt, $3\text{SbBr}_5 \cdot 2\text{GlBr}_2 \cdot 18\text{H}_2\text{O}$, forms black, glistening prisms and is very unstable. The *aluminium* salt, $5\text{SbBr}_5 \cdot 2\text{AlBr}_3 \cdot 24\text{H}_2\text{O}$, forms black, glistening, stout prisms, and is less hygroscopic than the glucinum salt.

The *rubidium* salt from antimony tetrabromide, Rb_2SbBr_6 , forms small, black, six-sided tablets, and only slowly loses bromine.

Vanadium antimony bromide, $\text{SbBr}_3 \cdot \text{VBr}_4 \cdot 7\text{H}_2\text{O}$, forms black, pointed, hygroscopic prisms, and is decomposed by water.

T. M. L.

Precipitation of Crystalline Gold by Formaldehyde. NICOLAI AWERKIEFF (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 828—835).—From solutions of gold chloride or bromide containing 0.01 gram of gold per

litre and strongly acidified with nitric or hydrochloric acid, formaldehyde precipitates nearly the whole of the gold in a crystalline condition. The precipitation takes place in the cold, but proceeds more rapidly when the solution is heated. The crystals have a length of from 0.2—0.9 mm. and represent mostly combinations of cubic and octahedral forms, although other forms are, in some cases, met with; two sp. gr. determinations at 20° gave the values 19.4278 and 19.4341. From acidified solutions of mixtures of gold chloride with salts of copper, antimony, mercury, zinc, lead, manganese, tin, arsenic, and the metals of the first and second groups, formaldehyde only precipitates the gold. From very dilute solutions containing less than 0.005 gram of metal per litre, platinum is very slowly precipitated by formaldehyde.

T. H. P.

Action of Certain Salts on Platinic Chloride. WILLIAM ECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1902, 730—731).—Dilute aqueous solutions containing manganous sulphate and platinic chloride undergo no change on keeping in the dark or in diffused daylight; on exposure to sunlight, a small quantity of platinous chloride is formed, but no change occurs with manganous chloride under the same conditions. Similar solutions of uranous sulphate and platinic chloride are not altered when kept in the dark or in diffused light, but oxidation to uranic sulphate takes place in sunlight.

G. D. L.

Complex Salts of Hexavalent Osmium. L. WINTREBERT (*Ann. Chim. Phys.*, 1903, [vii], 28, 15—144).—Two different methods of estimating osmium in its compounds are employed, according as the whole of the osmium is left as metal when the compound is heated in a current of hydrogen, or the osmium is partially volatilised as osmium tetroxide. With the compounds of the first class, the residue may consist only of osmium, which can be directly weighed, or it may consist of osmium mixed with some other material. If the latter is soluble in water, the reduction of the osmium compound is carried out in a glass tube which has a constriction, where a plug of asbestos is fixed, so that the osmium may be washed with water *in situ*, and then dried in a current of carbon dioxide and weighed. The same method may be used if the material mixed with the osmium is soluble in hydrochloric acid. When in the reduction of the osmium compound, alkali hydroxides are formed together with the osmium, the reduction must be carried out in a platinum boat, and the product subsequently transferred to the glass tube. In the presence of silver, the osmium must be volatilised in the form of tetroxide. Those substances in which, on ignition, a certain amount of the osmium is volatilised as tetroxide, must be heated with anhydrous sodium carbonate in hydrogen in the glass tube. Nitrogen and carbon contained in osmium compounds are estimated by burning the substance mixed with tungstic acid in an exhausted combustion tube in the presence of copper oxide and reduced copper.

Osmyl salts, $M_2OsO_2X_4$ (where M is a univalent metal and X a univalent acid radicle), the osmylnitrites, osmyloxalates, and osmylchlorides can all be prepared from the tetroxide (or potassium osmate) and the acid (nitrous, oxalic, hydrochloric) in the presence of excess of alkali, or, better, by acting on an alkaline solution of the osmate with the acid: $K_2OsO_4 + 4HX = K_2OsO_2X_4 + 2H_2O$. The osmylnitrites are converted into the oxalates by oxalic acid, and the latter into the chlorides (or bromides) by hydrochloric (or hydrobromic) acid; the reverse series of changes is induced by the potassium salts of the acids. Hydriodic acid converts all these compounds into osmates. The osmyl salts are unstable in aqueous solution, decomposing according to the equation: $M_2OsO_2X_4 + 2H_2O = H_2OsO_4 + 2MX + 2HX$, but they are stable in the presence of excess of acid; in the case of osmylnitrites, the tetroxide is formed and not the acid, H_2OsO_4 , as the nitrous acid acts as an oxidising agent. Excess of potassium hydroxide converts the osmyl salts into osmates: $K_2OsO_2X_4 + 4KOH = K_2OsO_4 + 4KX + 2H_2O$; whilst ammonia produces a precipitate of tetra-ammonio-osmyl salts: $M_2OsO_2X_4 + 4NH_3 = OsO_2(NH_3)_4X_2 + 2MX$. Hot concentrated hydrochloric acid changes the osmyl salts into osmichlorides: $K_2OsO_2X_4 + 8HCl = K_2OsCl_6 + 4HXC1 + 2H_2O$; a mixture of hydrochloric and nitric acids causes the production of osmyl chloride; concentrated hydrobromic and hydriodic acids act on the osmyl salts (with the exception of the osmylchlorides) in the same way.

Potassium osmylnitrite, $K_2OsO_2(NO_2)_4$, crystallises in unstable, orange-red prisms; *osmyltetra-ammonio-nitrite*, $OsO_2(NH_3)_4(NO_2)_2$, is an unstable, yellow, crystalline powder, which is, however, unlike other osmyl salts in that it is not attacked by hydrogen haloids.

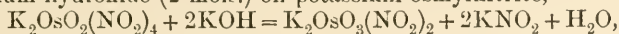
The following new osmyloxalates are described (compare Abstr., 1900, i, 543; 1901, i, 313; 1902, i, 587): *ammonium osmyloxalate*, $(NH_4)_2OsO_2(C_2O_4)_2 \cdot 2H_2O$, is isomorphous with the potassium salt (*loc. cit.*), triclinic [$a : b : c = 0.4995 : 1 : 1.0451$], but is far more soluble in water, 100 parts of water at 15° dissolving 10 parts of the ammonium salt, but only 0.75 parts of the potassium salt; the *magnesium* and *calcium* salts are golden-yellow, crystalline powders, the *methylanmonium* and the *ethylammonium* salts crystallise in brown needles; these four salts all crystallise with $2H_2O$; the *silver* salt forms transparent, brown needles; barium forms two salts, $BaOsO_2(C_2O_4)_2 \cdot 4H_2O$ and $Ba_2OsO_2(C_2O_4)_3 \cdot 6H_2O$; the former salt crystallises in unstable, greenish-yellow needles and the latter in brownish-yellow, rhombic plates; the *strontium* salt forms a crystalline powder with $4H_2O$.

The osmylchlorides are prepared by the action of hydrochloric acid on the osmylnitrites; the *potassium* salt, $K_2OsO_2Cl_4$, crystallises in anhydrous, red octahedra, decomposed by water, and with $2H_2O$ in pale brown, triclinic crystals [$a : b : c = 0.5882 : 1 : 1.1795$]. The *ammonium* salt is anhydrous, and closely resembles, and is isomorphous with, the potassium salt.

Potassium osmylbromide, $K_2OsO_2Br_4 \cdot 2H_2O$, forms red, triclinic crystals, isomorphous with those of the hydrated chloride [$a : b : c =$

0.6015:1:1.2987]; the corresponding *ammonium* salt is unstable, decomposing into the osmibromide.

The osmyloxy-salts, $M_2OsO_3X_2$, are prepared by the action of excess of potassium nitrite on osmium tetroxide; $OsO_4 + 3KNO_2 = K_2OsO_3(NO_2)_2 + KNO_3$, by the regulated action of oxalic, hydrochloric, or hydrobromic acids on ammonium osmyloxynitrite, by the action of potassium hydroxide (2 mols.) on potassium osmylnitrite,



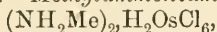
or, better, by the action of potassium nitrite or potassium osmate on the osmylnitrite. The osmyloxy-salts are sparingly soluble and are converted by the hydrogen haloids into osmi-chlorides, -bromides, and -iodides. They are changed into the osmyl salts by the regulated action of acids thus: $K_2OsO_3(NO_2)_2 + 4HX = 2HNO_2 + H_2O + K_2OsO_2X_4$ and $(NH_4)_2OsO_3(C_2O_4) + H_2C_2O_4 = (NH_4)_2OsO_2(C_2O_4)_2 + H_2O$.

Potassium osmyloxynitrite, $K_2OsO_3(NO_2)_2 \cdot 3H_2O$, crystallises in nearly black, monoclinic needles [$a : b : c = 1.0923 : 1 : 0.8682$; $\beta = 79^\circ 8' 30''$]; the *ammonium* salt is an anhydrous, yellow, crystalline powder; the *silver* salt, with H_2O , forms black crystals, the *barium* and the *strontium* salts, brown crystals with $4H_2O$ and $3H_2O$ respectively.

Of the osmyloxyoxalates, the *potassium* salt, which forms nearly black crystals with $2H_2O$, and the *ammonium* salt, which is an anhydrous, yellow, crystalline powder, are described.

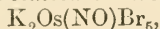
Ammonium osmyloxychloride, $(NH_4)_2OsO_3Cl_2$, and the corresponding *osmyloxybromide*, are yellow, crystalline powders.

The osmichlorides, -bromides, and -iodides are prepared by the action of concentrated hydrogen haloids on the alkali osmyloxynitrites; the salts of the alkaline earths give, however, the chlorides of the metals and osmic chloride, $OsCl_4$. *Methylammonium osmichloride*,



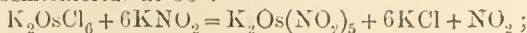
prepared from the osmyloxalate and hydrochloric acid, crystallises in pale red, hexagonal plates; the *ethylammonium* salt resembles the methylammonium salt. *Methylammonium* and *ethylammonium osmibromides* very closely resemble the potassium osmibromide. *Potassium osmi-iodide*, K_2OsI_6 , crystallises in soluble, violet-black octahedra; the corresponding *ammonium* salt forms blue-black octahedra.

Potassium nitroso-osmichloride is formed by the action of boiling concentrated hydrochloric acid on the osminitrite: $2K_2Os(NO_2)_5 + 10HCl = 2K_2Os(NO)Cl_5 + 3NO + 5NO_2 + 5H_2O$; it crystallises in red, rhombic crystals [$a : b : c = 0.9640 : 1 : 1.5123$], is isomorphous with potassium nitrosoruthenichloride, and is extremely stable both towards nitric acid and ammonia. *Potassium nitroso-osmibromide*,



crystallises in reddish-brown, rhombic prisms [$a : b : c = 0.96968 : 1 : 1.50417$]; the corresponding *iodide* crystallises in nearly black prisms, isomorphous with the salts just described.

Potassium osminitrite, $K_2Os(NO_2)_5$, is formed by the action of excess of a concentrated solution of potassium nitrite on a solution of potassium osmichloride at 80° :



if air is not excluded, osmium tetroxide and potassium osmyloxynitrite are formed ; the osminitrite forms very stable, triclinic, amber-yellow, hygroscopic crystals.

K. J. P. O.

Mineralogical Chemistry.

Composition of the Gas from the Fumerolles of Mont Pelée: Origin of Volcanic Phenomena. ARMAND GAUTIER (*Compt. rend.*, 1903, 136, 16—20).—The gas from the fumerolles of Mont Pelée, as analysed by Moissan (this vol., ii, 155), has practically the same composition as the gas obtained by the author by heating granite, porphyry, and other primary rocks to incipient redness (Abstr., 1901, ii, 171). It is noteworthy that the stones ejected from the volcano consist mainly of an andesite rich in hypersthene. The author's researches (Abstr., 1901, ii, 63, 92, 322) have, in fact, shown that the action of heat on the older rocks liberates not only water vapour but also hydrogen, hydrogen sulphide, carbon oxides, and hydrocarbons in relatively large quantity. A cubic kilometre of granite heated to redness would yield 26,640,000 tonnes of water and 6,700,000,000 cubic metres of gas at 15°. It follows that the heating to redness of moderately large masses of older rocks as a result of movements of the earth's crust, is capable of liberating immense volumes of water vapour and of gases, mostly inflammable, and thus producing violent volcanic disturbances, and it is unnecessary to assume the sudden inrush of masses of sea water into the hotter parts of the earth's crust in order to explain such phenomena.

C. H. B.

Some Springs of Mineral Gas. CHARLES MOUREU (*Compt. rend.*, 1902, 135, 1335—1337).—Five springs in the Pyrenees from which gases are evolved have been investigated. All of these contained nitrogen, carbon dioxide, oxygen, and argon. The following amounts of argon were found : in the Peyré spring at Ogeu, 0.9 per cent. by volume ; in the Nehe spring at Dax, 1.6 per cent. ; in the Trou des Pauvres spring at Dax, 1.2 per cent. ; in the Vieille spring at Eaux-Bonnes, 1.8 per cent. ; and in the Saint Augustin spring at Panticosa, 1.2 per cent. Deslandres made a special spectroscopic examination of these gases, and found that the gas from the Saint Augustin spring contains helium. Some spectroscopic lines were also observed which do not belong to argon or helium, and these are being further investigated.

J. McC.

A New Member of the Rhombohedral Carbonate Group. A. JOHNSON (*Centr. Min.*, 1903, 13—15).—A rose-red mineral associated with chalybite, pyrites, and quartz from Eiserfeld, near Siegen, was found to have the following composition :

MgO.	MnO.	FeO.	CoO,(NiO).	CO ₂ .	H ₂ O.	Total.
33·41	7·50	6·50	5·12	46·77	0·31	99·61

which corresponds with :

MgCO ₃ .	MnCO ₃ .	FeCO ₃ .	CoCO ₃ .	Total.
70·16	12·14	10·47	8·12	100·89

Measurement of angle between the curved cleavage faces gave $rr' = 72^{\circ}19'$ (approx.) ; sp. gr. = 3·15. L. J. S.

Occurrence of a Manganese Silicate containing Carbonate in the Aure Valley in the Pyrenees. HERMANN LIENAU (*Chem. Zeit.*, 1903, 27, 14—15).—Two manganese ores, which have been previously described (*ibid.*, 1899, 23, 418), viellaurite (consisting of 51 per cent. dialogite and 49 per cent. tephroite) and torrensitite (consisting of 51·5 per cent. rhodonite, 45 per cent. dialogite, and 3 per cent. water), are held by Lacroix not to be homogeneous minerals. Three new minerals have been found in the Aure valley in the Pyrenees, *lacroixite* (consisting of 81·4 per cent. dialogite and 18·6 per cent. rhodonite), *chocolate stone* (of 53 per cent. tephroite, 36 per cent. hausmannite, 10 per cent. dialogite, and 1 per cent. water), and *huelvite* (consisting of 71 per cent. dialogite, 27 per cent. tephroite, and 2 per cent. water). These five minerals may be regarded as the result of different degrees of weathering of rhodonite, MnSiO_3 ; thus torrensitite, $\text{MnCO}_3, \text{MnSiO}_3$, *lacroixite*, $5\text{MnCO}_3, \text{MnSiO}_3$, *huelvite*, $2\text{MnCO}_3, 3\text{Mn}_2\text{SiO}_4$, *viellaurite*, $5\text{MnCO}_3, 2\text{Mn}_2\text{SiO}_4$, *chocolate stone*, $2\text{MnCO}_3, 5\text{Mn}_2\text{SiO}_4, 3\text{Mn}_2\text{MnO}_4$. K. J. P. O.

[Felspar from Asia Minor.] LUDWIG MILCH (*Jahrb. Min.*, 1903, Beil.-Bd., 16, 110—165).—In a petrographical description of the volcanic rocks (dacites, andesites, and basalts) of the Galatian andesite region, north of Angora, is given the following analysis, by H. Schäfer and Herz, of felspar isolated from the ground-mass of a mica-dacite :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ , FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
70·7	16·0	2·8	0·2	1·1	5·0	1·5	0·9	98·2

L. J. S.

Stone Implements and their Rough Material from Swiss Lake Dwellings. A. BODMER-BEDER (*Jahrb. Min.*, 1903, Beil.-Bd., 16, 166—198).—Detailed petrographical descriptions are given of about a hundred specimens of stone implements and of the rough

material from which they were fashioned. The following analyses, by H. Hirschy and Miss L. Hezner, are given: I—III, nephrite axes; IV and V, jadeite axes; VI, chloromelanite axe; VII, axe of chloromelanitic pyroxenite; VIII, harzburgite from the St. Gotthard tunnel; IX, serpentine axe; X and XI, serpentine from the Gurschen-alp in the St. Gotthard district:

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.
I.	53.21	trace	2.49	4.98	1.02	—	11.09
II.	57.37	—	0.85	0.16	5.65	—	11.72
III.	58.37	—	0.50	1.40	1.38	—	13.32
IV.	58.41	0.17	21.35	1.31	0.31	—	3.45
V.	58.39	0.13	22.77	2.42	0.27	trace	1.70
VI.	55.11	0.36	13.49	10.09	1.52	0.45	5.05
VII.	57.86	0.57	21.23	4.01	1.05	—	2.04
VIII.	40.40	trace	2.63	4.31	4.98	—	1.74
IX.	39.09	trace	3.49	4.78	2.94	trace	1.43
X.	40.42	trace	1.09	2.59	2.25	—	2.31
XI.	41.47	trace	2.07	5.10	0.95	—	0.25

	MgO.	K ₂ O.	Na ₂ O.	H ₂ O <110°.	H ₂ O >110°.	Total.	Sp. gr.
I.	23.51	trace	0.76	0.71	2.81	100.58	2.982
II.	22.37	—	—	0.25	1.98	100.35	3.080
III.	23.28	—	—	0.20	2.02	100.47	2.996
IV.	2.01	0.77	12.03	0.09	0.31	100.21	3.361
V.	1.27	0.27	12.39	0.08	0.24	99.93	3.418
VI.	2.54	0.37	11.42	0.11	0.24	100.75	3.418
VII.	2.85	2.06	8.35	0.05	0.24	100.31	3.452
VIII.	40.37	—	—	0.02	5.33	99.78	3.073
IX.	35.94	trace	trace	0.27	11.37	99.31	2.677
X.	37.24	—	—	0.51	13.73	100.14	2.623
XI.	38.89	—	—	0.14	11.61	100.48	2.534

L. J. S.

Chemical Changes in Contact-metamorphism. K. DALMER (*Centr. Min.*, 1903, 15—17).—The mineral changes which take place when phyllites and clay-slates are altered by contact-metamorphism to andalusite-mica-rocks are expressed by new equations simpler than those previously given by the author (*Abstr.*, 1898, ii, 82, 171).

L. J. S.

Volcanic Dust from Martinique. LUDWIG SCHMELCK (*Chem. Zeit.*, 1903, 27, 34).—The following analyses have been made of volcanic dust from Mont Pelée: (I) deposited on board the English steamer "Coya," which was at the time of the eruption 200—250 miles from the island of Martinique; (II) collected at St. Pierre; they may be compared with (III) volcanic dust from St. Vincent:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	TiO ₂ .	P ₂ O ₅ .	SO ₃ .	MnO.
I.	57.75	17.7	2.84	2.73	8.11	3.51	0.94	5.03	0.7	trace	trace	trace
II.	55.40	15.55	5.55	3.89	8.26	3.51	0.53	5.28	1.0	trace	0.35	trace
III.	55.08	18.0	2.46	4.57	7.74	3.34	0.65	3.45	0.8	0.17	0.24	0.21

Carbonate was absent from all the specimens; I and II lost 1 per cent. and 1.3 per cent. respectively on ignition; III lost 2.05 per cent. water on heating. The analysis of the dust from St. Vincent was made by Hillebrand (*Amer. J. Sci.*, 1902, 327).

K. J. P. O.

Physiological Chemistry.

A New Product of Pancreatic Autodigestion. FRITZ BAUM (*Beitr. chem. Physiol. Path.*, 1903, 3, 439—441). **Scatosine.** ROBERT E. SWAIN (*ibid.*, 442—445).—After the pancreas has been allowed to digest itself for five or six weeks, among the materials which can be separated from the alcoholic extract by benzoyl chloride is one of the formula $C_{10}H_{12}N_2O_2(C_7H_5O)_4$, which crystallises in colourless needles, melts at 169°, dissolves sparingly in ether, and is insoluble in benzene. By fusing with alkali, a strong, scatole-like smell is produced. When the benzoyl compound is saponified, the free base *scatosine*, $C_{10}H_{16}N_2O_2$, is precipitable by phosphotungstic acid, and gives a yellow precipitate with bromine water. Three grams of it were obtained from 20 pancreases.

The second paper points out that scatosine is also found as a decomposition product of other proteids, that it is not identical with tryptophan ($C_{11}H_{12}O_2N_2$, Hopkins and Cole), and from the examination of its hydrochloride concludes that the formula given above is correct. It contains two NH_2 and two OH groups.

W. D. H.

Action of Sodium Carbonate on Monobutyrin. MAURICE DOYON and ALBERT MOREL (*Compt. rend. Soc. Biol.*, 1902, 54, 1524—1525).—Blood serum does not saponify neutral fats; Hanriot states, however, that it saponifies monobutyrin; the lipase to which this is due should be called monobutyrynase. He further states that the activity of the ferment is enhanced by sodium carbonate, but this is disputed in the present paper; sodium carbonate by itself, however, produces saponification, even when dilute, at the usual incubator temperature.

W. D. H.

Digestibility of Carbohydrates. Estimation of Starch in the Presence of Pentosans. ST. WEISER and A. ZAITSCHER (*Pflüger's Archiv*, 1902, 93, 98—127).—In the ordinary process of estimating starch in flours, &c., by inversion with hydrochloric acid, a

certain amount of pentosan is formed. The latter must be separately estimated, and, as pentosans reduce Fehling's solution to the same extent as dextrose, the copper reducing power of the inverted starch solution should be corrected by a corresponding amount to ascertain the true amount of starch present.

Digestion experiments on a number of oxen, sheep, pigs, poultry, &c., were made, the starch and pentosans being estimated both in the food and excrements. The average results showed that oxen digested 63.4 per cent. of the pentosans; sheep, 53.6 per cent.; horses, 45.5 per cent.; pigs, 47.9 per cent.; and poultry, 23.9 per cent. The starch was almost completely assimilated in every case.

W. P. S.

Chemistry of Fatigue. HENRY WINSTON HARPER and MARGARET HOLLIDAY (*J. Amer. Chem. Soc.*, 1903, 25, 33—47).—The subject of the experiment received a diet containing milk, eggs, butter, bread, Malta-vita, sugar, lemons, and sometimes a banana, so arranged to maintain nitrogen equilibrium. The experiment included three periods of three days: (1) period of rest, (2) period of excessive exercise (a hurdle race until the subject fell exhausted), and (3) a second period of rest. The total nitrogen was determined in the urine and faeces as well as the nitrogen as ammonia and uric acid, and the nitrogen in the xanthine silver precipitate, in the phosphotungstic acid precipitate, and in the filtrate. The amounts of phosphoric, sulphuric, and hydrochloric acids in the urine were also determined.

In the food consumed, the amount of nitrogen was greatest in the first period and least in the second. The total nitrogen assimilated was greatest in the third and least in the second period. The action of the digestive tract on the nitrogenous food was greatest in the second and least in the first period. There was a decided loss of nitrogen during the middle period and a gain in both others, especially in the third; the whole nine days' experiment resulted in a slight gain in nitrogen.

The output of phosphoric acid was greatest in the first and least in the last period. In the case of sulphuric acid, the output was also least during the third period, but was greatest in the second period. Chlorine showed a marked decrease during the second period and a rise in the third, although the amount of sodium chloride consumed was the same.

Evidence was obtained of the presence of methyl derivatives of xanthine in the urine.

N. H. J. M.

Iodine in the Thyroid. W. A. NAGEL and ERNST ROOS (*Chem. Centr.*, 1903, i, 183; from *Arch. Anat. Physiol., physiol. Abth.*, 1902, 267—277).—After extirpation of the greater part of the thyroid gland, the percentage of iodine increases in the remainder (for instance, from 0.8 per 1000 to 1.43 per cent.). If only half the gland is excised, this does not take place. Pregnancy causes an increase (for instance, from 0.5 to 2.5 per 1000). The administration of pilocarpine or of a bromine compound makes no difference.

W. D. H.

Composition of Goose Fat. ST. WEISER and A. ZAITSCHEK (*Pflüger's Archiv*, 1902, 93, 128—133).—The composition of the fat obtained from geese fed on Indian millet (broom corn) and maize was not found to differ from that of normal goose fat. Although the geese increased considerably in weight, the increase being almost entirely due to fat, investigation showed that the latter was not obtained from the fat in the food, but was formed from assimilated carbohydrates.

W. P. S.

New Method of producing Hæmolysins. M. ARMAND RÜFFER and MILTON CRENDIROPOULOS (*Brit. Med. J.*, 1903, i, 190—191).—If human urine is injected two or three times subcutaneously into a rabbit, the serum obtained from the rabbit acquires a marked hæmolytic action on human red blood corpuscles. Schatten Groh (*Centr. allg. Pathol.*, 1902, 13, No. 14) has also found that the serum similarly obtained has agglutinating and hæmolytic, but no precipitating, properties. The specificity of such serum is not absolute.

W. D. H.

Precipitins and Lysins. FRANZ FUHRMANN (*Beitr. chem. Physiol. Path.*, 1903, 3, 417—432).—The proteids of serum were divided into three fractions by the method of fractional precipitation with ammonium sulphate; one-third saturation precipitates euglobulin; one-half saturation precipitates pseudo-globulin, and, finally, complete saturation precipitates serum-albumin.

The 'precipitin' action of the lacto-serum of the rabbit in relation to milk, caseinogen solutions, and ox serum, is in the euglobulin fraction. Normal rabbit's serum has no rennet-like action on milk, but the euglobulin separated out from this serum has.

The hæmolytic action of rabbit's serum immunised against ox-blood is found in both globulins, but not in the albumin.

"Complementary" actions are not discoverable in solutions of the proteids separated out as above from normal rabbit's serum. The hæmolytic action of pseudo-globulin from rabbit's lysin-serum is different from that of euglobulin, for, in the latter, a substance is also present which acts inhibitingly on the process of hæmolysis (anti-complement). The anti-complement is rendered inactive by heating to 56°. It is not influenced by the addition of ammonium sulphate, and so differs from the complements of normal serum and of lysin-serum, which are very sensitive towards this salt. This accounts for the absence of complement action in the proteid fractions.

The euglobulin of lysin-serum shows, in addition to its lysin action, a precipitin action also in relation to caseinogen solution, cows' milk, ox serum, and euglobulin of ox serum; it has no effect on the pseudo-globulin of ox serum. After immunising animals with solutions of euglobulin, or pseudo-globulin, the immune serum has a marked precipitin action towards the respective proteids.

W. D. H.

Iron in Normal and Pathological Human Urine. ALBERT NEUMANN and ARTHUR MAYER (*Zeit. physiol. Chem.*, 1902, 37, 143—148).—Neumann's iodometric method of estimation was used

(this vol., ii, 243). In normal urine, the average daily quantity of iron is 0.983 mg. In ten cases of pathological urine from various diseases, this was found to be increased; in one case of liver cirrhosis to 2, and in the case of a drinker to 6—8, mg. per diem. In diabetes (another 6 cases), the average was 4.1 mg. per diem, and the amount is proportional to that of the sugar. Various forms of nuclei contain both iron and a carbohydrate radicle; it is suggested that metabolism of nuclei will explain the result.

W. D. H.

Physiological Action of Betaine. KARL ANDRLIK, A. VELICH, and VL. STANĚK (*Chem. Centr.*, 1903, i, 182—183; from *Centr. Physiol.*, 16, 452—454).—The old statement that betaine is non-toxic is confirmed. After intravenous injection, it appears in the dog almost completely in the urine. If given by the mouth, about a third is recoverable from urine and faeces. None, however, was found in the excreta of a cow which had been fed on it. Staněk's method of estimation was used; in this, the urine is heated with sulphuric acid at 130°; from the residue, 82 per cent. of betaine added to the urine can be recovered.

W. D. H.

Behaviour of Halogen-substituted Toluenes and Amino-benzoic Acids in the Organism. HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1902, 3, 365—372. Compare Abstr., 1901, ii, 614).—Feeding experiments with *o*-, *m*-, and *p*-chloro- and bromo-toluenes have shown that in the case of the dog these compounds are all oxidised and excreted in the form of hippuric acids. *p*-Chlorohippuric acid, $C_6H_4Cl \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H, H_2O$, was thus obtained from *p*-chlorotoluene; it melts at 143° and, on hydrolysis with concentrated hydrochloric acid, gave *p*-chlorobenzoic acid (m. p. 235°). *o*-Chlorohippuric acid was isolated in the form of its calcium salt, from which *o*-chlorobenzoic acid (m. p. 137°) was obtained. *o*-Bromohippuric acid, $C_6H_4Br \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H, H_2O$, melts at 153°. *m*-Bromohippuric acid was obtained from the urine of a dog fed on *m*-bromobenzoic acid; it crystallises with H_2O and melts at 183°.

In the case of rabbits, the chlorotoluenes were oxidised and excreted as benzoic acids; the bromotoluenes, on the other hand, were converted into hippuric acids, the ortho-compound completely and the meta- and para- partially. The chloro- and bromo-toluenes act as poisons towards rabbits, as do also the chloro- and bromo-benzoic acids, the para-compound being the most active and the ortho- the least; the bromo- are more poisonous than the chloro-derivatives.

Aminobenzoic acids are excreted unchanged; they are powerful poisons, the ortho-compound being the most active.

K. J. P. O.

Phloridzin and Experimental Glycosuria. KARL SPIRO and HANS VOGT (*Chem. Centr.*, 1903, i, 180—181; from *Verhandl. Kongr. inn. Med.*, 1902, 524—526).—A number of experiments consisting in the injection of various sugars and salts into the blood stream are de-

scribed, and the effect then produced by the administration of phloridzin. The main conclusion drawn is that phloridzin diabetes is due to disorder of the kidneys.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A Colourless Bacterium, the Carbon Food of which comes from the Atmosphere. MARTINUS W. BEYERINCK and A. VAN DELDEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 398—413).—When a solid or liquid nutrient medium free from carbonaceous matter is inoculated with garden soil, a thin film of a white or feebly rose-coloured culture of *Bacillus oligocarbophilus* develops on it in the dark in the course of two or three weeks, provided the air has free access. The nitrogen required for its life process may be derived from ammonium salts or from nitrites; in presence of nitrifying organisms, it does not develop. The carbon required for its development is assimilated from the atmosphere, and it has been proved that carbon dioxide cannot serve as its food. The nature of the carbon compound in the air which this bacterium absorbs has not been settled, but it may be that discovered by Karsten in 1862, and recently alluded to by Henriët (*Compt. rend.*, 1902, 135, 89, 101). The amount of carbon assimilated from the atmosphere has been roughly estimated by direct weighing and by titration with permanganate.

J. McC.

Decomposition of Proteids by means of Bacteria. OSKAR EMMERLING (*Zeit. physiol. Chem.*, 1902, 37, 180).—In reply to Taylor, (this vol., ii, 169), the author refers to his previous work (*Abstr.*, 1897, ii, 113; 1902, ii, 279).

J. J. S.

Presence of a Kinase in some Basidiomycetes. C. DELEZENNE and H. MOUTON (*Compt. rend.*, 1903, 136, 167—169).—An extract of *Amanita muscaria* in presence of the pancreatic juice of a dog, digested about 1 gram of albumin in 12—36 hours. The liquid loses its kinasic properties when heated at 100° for 10 minutes or at 70° for half an hour. When precipitated with alcohol and redissolved in water, the solution has the same properties as the original extract, but prolonged contact with alcohol renders the product less active.

Similar results were obtained with *Amanita citrina*; the extract is, however, more feeble in its action than that of *A. muscaria*. *Hypholoma fasciculare* is fairly active, *Psaliota campestris* and *Boletus edulis* extremely feeble, whilst *Hydnum repandum* is completely inactive.

N. H. J. M.

Biology of some of the Moulds occurring in Dairy Products. KURT TEICHERT (*Milch-Zeit.*, 1902, 31, 801—803).—The results are given of experiments concerning the growth of *Oidium*

lactis, *Penicillium glaucum*, and *Mucor mucedo* on sugar solutions and on nitrogenous media containing various sugars. *Penicillium glaucum* attacked sugars the most powerfully, the products formed being of an acid nature. *Oidium lactis* had the least action. The latter mould, when grown upon media containing levulose, caused alcoholic fermentation to take place, an intense odour of ethyl malate being produced at the same time.

W. P. S.

Influence of the Stereochemical Configuration of Glucosides on the Activity of Hydrolytic Diastases. HENRI POTTEVIN (*Compt. rend.*, 1903, 136, 169—171).—*Schizo-Saccharomyces Octosporus* (Beyerinck) and *Mucor alternans* ferment maltose and methyl-*d*-glucoside, but are without action on sucrose and α -methyl-*d*-fructoside. *Aspergillus niger*, cultivated on normal Raulin solution with sucrose, yielded, when macerated with chloroform water, a solution of ferments which acted on amygdaline and on β -*d*-glucosides, but not on the two methyl-*d*-galactosides or on lactose.

The ferments of lactose known as Duclaux, Kayser, and Adametz yeasts, ferment lactose and β -methyl-*d*-galactoside; when ground, they yield a diastase which acts on the two galactosides.

N. H. J. M.

Action of Magnesium Salts on the Lactic Acid Fermentation. CHARLES RICHET (*Compt. rend. Soc. Biol.*, 1902, 54, 1436—1438).—Fresh experiments are given to show that magnesium salts favour the lactic acid fermentation; 12.5 grams of magnesium chloride per litre is the most favourable quantity.

Much of the paper is polemical against Aloy and Bardier (*Arch. internat. Pharmacod. et de Therap.*, 1902, 10, 399—413). W. D. H.

Formation of Substances with a Strong Taste by the Action of Yeast on Proteids. THOMAS BOKORNY (*Chem. Zeit.*, 1903, 27, 5—7).—In recent times, substances have been extracted by means of alcohol from yeast on the large scale which have a taste resembling that of meat extract. It has been found that the yield of such an extract is largely increased by carefully drying the yeast, when proteolysis takes place. The yield is still further increased when yeast is kept at 35° in the presence of 1 per cent. phosphoric or lactic acids. If proteid be added to yeast under these conditions, it is largely converted by a proteolytic enzyme into soluble albumoses and peptones, the quantity of the substance with strong taste, however, not being markedly increased. It is suggested that this proteolytic action of yeast may find an important technical application.

K. J. P. O.

Alcoholic Fermentation. I. R. O. HERZOG (*Zeit. physiol. Chem.*, 1902, 37, 149—160).—The velocity of the hydrolysis of dextrose and of levulose in the presence of commercial zymase has been determined. The amount decomposed in any given time was estimated by driving over the carbon dioxide by a stream of air. The numbers obtained by using the equation for a unimolecular reaction, come out practically

constant. Henri's equation, $K^1 = 1/2t(\log a + x/a - x)$, does not give such good results.

Bredig and Müller von Berneck's (Abstr., 1900, ii, 213) equation, $K_1/K_2 = (c_1/c_2)^b$, also holds good, b being equal to 2.

The influence of temperature on the velocity is also similar to that observed in other catalytic actions (Van't Hoff-Arrhenius, *Zeit. physiol. Chem.*, 1889, 4, 226). In all these points, there is perfect harmony between the alcoholic fermentation of dextrose by zymase and ordinary catalytic actions. J. J. S.

Effects of Fermentation on the Composition of Cider and Vinegar. CHARLES A. BROWNE, jun. (*J. Amer. Chem. Soc.*, 1903, 25, 16—33).—Analyses of cider were made the day after pressing and subsequently at intervals of two weeks. The period of greatest chemical activity is from the fourth to the seventh week. Whilst the sucrose disappeared after about two months, and the dextrose after about four months, a small amount of lævulose remained unaffected owing to alcoholic fermentation being checked by the production of acetic acid. During the period of alcoholic fermentation, the acetic acid slowly increases, whilst the fixed (malic) acid diminishes in quantity. Nearly 89 per cent. of the theoretically possible amount of alcohol was produced; about 30 per cent. of the deficiency is attributed to loss by evaporation.

The same cider was employed in subsequent experiments on acetification. The yield of acetic acid was 89.2 per cent. of the theoretical yield, the deficiency being attributed partly to loss by evaporation and partly to destruction of acetic acid by *Bacterium xylinum* or an allied form.

During the deterioration of the vinegar, there was an increase in the amount of reducing substances. By treatment with phenylhydrazine, two osazones were obtained, the one melting at 142—143° (probably phenylformosazone) and the other identical with von Pechmann's diacetylosazone.

The dried sediment formed during the alcoholic and acetic fermentation contained: water, 4.91; fat, 1.69; proteid, 20.13; crude fibre, 5.69; pentosans, 1.48; nitrogen-free extract, 64.93; and ash, 2.65 per cent. The ash contained 29.64 per cent. of phosphoric acid and 24.23 per cent. of silica. N. H. J. M.

Acetaldehyde in the Ageing and Alterations of Wine. AUGUSTE TRILLAT (*Compt. rend.*, 1903, 135, 171—173).—The ageing of wine is accompanied by a normal oxidation of the alcohols present. The production of aldehydes is increased under the influence of certain diseases, and, according to circumstances, the aldehydes enter into combination with the colouring matter of the wine, forming insoluble products, or are resinised by the mineral salts. N. H. J. M.

Inversion of Sugar in Plastered Wines. GAETANO MAGNANINI and A. VENTURI (*Chem. Centr.*, 1903, i, 186—187; from *Staz. sperim. agrar. ital.*, 35, 714—725).—Experiments made to decide the question whether the action of calcium sulphate on the potassium hydrogen

tartrate in wines results in the formation of free tartaric acid, calcium tartrate, and potassium sulphate (Chancel) or merely of calcium tartrate and potassium hydrogen sulphate (Bussy and Buignet).

From the slow inversion of cane sugar in such wines at 70°, the authors conclude that there cannot be any notable quantity of potassium hydrogen sulphate.

L. DE K.

Isolation of Crystallised Galactose from the Products of the Digestion of the Galactans of the Horny Albumen by Seminase. HENRI HÉRISSEY (*Compt. rend. Soc. Biol.*, 1902, 54, 1174—1176. Compare Abstr., 1900, ii, 233, and 561).—The presence of galactose in the products of digestion of the galactans from the horny albumen of leguminous plants was deduced from the fact that mucic acid was formed by the action of nitric acid on the sugars produced. It has now been placed beyond doubt by the actual preparation of pure galactose by the partial extraction with alcohol of the mixture of mannose and galactose obtained from the manno-galactan of *Melilotus leucantha*. It is probable that seminase itself contains several distinct enzymes.

A. H.

Influence of Formaldehyde on the Growth of some Fresh-water Algæ. RAOUL BOUILHAC (*Compt. rend.*, 1902, 135, 1369—1371).—*Nostoc* and *Anabæna*, when grown without sufficient light to enable them to decompose carbon dioxide, are able to utilise formaldehyde. The minimum amount of light required to enable the plants to polymerise formaldehyde is very close to the amount necessary for the decomposition of carbon dioxide.

N. H. J. M.

Investigations of Glucosides in Connection with the Internal Mutation of Plants. TH. WEEVERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 295—303).—The amount of glucoside was determined in extracts made with boiling water by estimating the sugar before and after treatment with emulsin for 24 hours.

The quantity of salicin in young buds of *Salix purpurea* greatly decreases, but rapidly increases when assimilation begins. In the case of branches kept in the dark, the new shoots were found to contain more than 7 per cent. of salicin, but as the shoots grew the amount diminished. Salicin is found in young leaves developing normally; it disappears for a moment and then reappears. Separated leaves lost 30 per cent. of the salicin during the night, but recovered the amount in the daytime. When the leaves were attached to branches, it was found that with the loss of salicin in the leaves there was coincidentally a gain in the bark during the night. These changes in the amount of salicin are accompanied by changes, but in the opposite direction, in the amounts of catechol present in the leaves and bark.

The conclusion is drawn that the decomposition of salicin takes place in every cell, the dextrose migrating towards the green parts, whilst catechol remains in the cell and combines with dextrose, coming from cells situated nearer to the bark, to form salicin. The amount of

catechol corresponds with the decrease in the absolute quantity of salicin.
N. H. J. M.

Influence of the Nature of External Media on the State of Hydration of Plants. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1903, 136, 160—163. Compare this vol., ii, 172).—Addition of mineral salts to the soil caused an acceleration of the diminution of the proportion of water in plants. The effect is analogous to that of very intense light (compare Berthelot, *Compt. rend.*, 1899, 128, 139). Nitrates cause the greatest loss of water, then sulphates, chlorides, and lastly, phosphates.
N. J. H. M.

Physiological Importance of Calcium in Plants. PAUL BRUCH (*Bied. Centr.*, 1903, 32, 39—44; from *Landw. Jahrb.*, 1901; *Suppl.*, iii, 127).—Water culture experiments in which wheat, buckwheat, *Elodea canadensis*, rye, barley, and oats were grown with and without calcium sulphate, and with strontium or barium sulphate instead of the calcium salt. In very few days, the roots of plants which had no calcium ceased growing and became brown, and the leaves of wheat, buckwheat, and rye soon died. In *Elodea*, there was an increased accumulation of starch in absence of calcium. Plants grown without calcium contained more potassium hydrogen oxalate than normal plants.

Strontium and barium had no effect in presence of sufficient calcium, but in absence of calcium they considerably increased the root-development, which was not much less than in solutions containing calcium; they had, however, no effect on leaf production.

Wheat plants grown in absence both of calcium and magnesium died much sooner than when only calcium was wanting,

As regards the supposed function of calcium in rendering oxalic acid harmless, it is shown that different plants vary considerably in their behaviour towards oxalic acid, and that in some cases oxalic acid is not poisonous, but beneficial.

It is shown that calcium forms compounds with dextrose, notwithstanding the presence of carbon dioxide; the presence of calcium does not, however, seem to increase the diffusibility of dextrose.

Experiments with different calcium salts showed that mono-calcium phosphate gave the best results in sand culture, but acts poisonously in water culture. Calcium nitrate and sulphate checked the growth of roots, whilst dicalcium and tricalcium phosphates were favourable.
N. H. J. M.

Hydrogen Cyanide in Sorghum. HENRY B. SLADE (*J. Amer. Chem. Soc.*, 1903, 25, 55—59).—Two analyses of sorghum showed that the stalks contained 0.013 and 0.014 per cent. of hydrocyanic acid. A kilogram of sorghum containing this quantity might prove fatal when consumed by cattle. The poison seems to be produced by the action of an enzyme on a glucoside, but attempts to isolate a glucoside were unsuccessful (compare Dunstan and Henry, *Abstr.*, 1901, i, 39, 647; 1902, ii, 578).
N. H. J. M.

The Fatty Oil of *Sambucus racemosa*. JULIUS ZELLNER (*Monatsh.*, 1902, 23, 937—941).—This oil, obtained from the fruit of *Sambucus racemosa*, on being warmed had a distinct elder-like odour, solidified at 3—4°, had a sp. gr. 0·9171 at 15°, n_D 1·472 at 20°, an acid number 3·15, and a saponification number 196·8. The liquid fatty acids (79 per cent.) consisted mainly of oleic and linoleic, whilst the solid fatty acids were mainly palmitic and arachidic. A. McK.

Presence of Sucrose in Almonds and its Rôle in the Formation of the Oil. C. VALLÉE (*Compt. rend.*, 1903, 136, 114—117).—Sucrose, reducing sugars, and oil were determined both in almonds and in the pericarp at different dates from March to October. Whilst the pericarp was found to contain relatively constant amounts of sugars (mainly reducing sugars), there is a progressive increase of sucrose in the almonds until the production of oil begins, after which there is a decrease. There is also a decrease (in the almonds) in the amount of reducing sugar coincident with the production of oil. The pericarp never contains more than traces of oil. The results indicate that there is either a production of sugars in the pericarp or else a constant migration, and that the sugars are utilised in the formation of the oil. N. H. J. M.

Relation between Leaf Venation and the Presence of certain Chemical Constituents in the Oils of the Eucalypts. R. T. BAKER and HENRY G. SMITH (*J. Roy. Soc. N. S. Wales*, 1902, 116—123).—The results of the authors' researches on the eucalypts of N. S. Wales have shown that there is a connection between the chemical constituents of the oils and the venation of the mature leaves of the several species, the genus being thus divided into fairly well-marked groups. Hence it is possible to suggest the probable constituents of the oil from an *Eucalyptus* by examining the venation of the leaves and, conversely, by chemical investigation of the oil to gain a clue to the species. E. G.

Can the Manurial Requirements of Plants be established by their Analysis? CONRAD VON SEELHORST, H. BEHN, and J. WILMS (*J. Landw.*, 1902, 50, 303—322. Compare *ibid.*, 1898, 109, and Abstr., 1899, ii, 609).—The amount of total nitrogen in the dry matter of a crop is the most important factor, and the relation of nitrogen to the ash constituents is of great importance in relation to the amounts of plant food in the soil. The amount of nitrogen assimilated depends, however, to a great extent on the climatic conditions which prevail in single months, and it seems to be impossible to establish relations between these conditions and the composition of the crop. The conclusion is drawn that the method is impracticable. N. H. J. M.

The Rôle of Plants in Dissolving the Undissolved Nutritive Substances of the Soil. P. KOSSOWITSCH (*Bied. Centr.*, 1903, 32, 44—49; from *J. exper. Landw.*, 1902, 165).—The dissolving action of plants is due to the carbon dioxide given off by the roots, and the

different amounts of insoluble phosphates dissolved in this manner are due, probably, to the different amounts of carbon dioxide furnished by the different varieties of plants.

At the same time, plants are able to supply themselves with phosphoric acid when present in extremely dilute solutions.

N. H. J. M.

Composition and Digestibility of Dried Potatoes. OSCAR KELLNER, JAKOB VOLHARD, and FR. HONCAMP (*Bied. Centr.*, 1903, 32, 50—52; from *Deut. landw. Presse*, 1902, 39, 691).—The dried potatoes contained: water, 6.95; crude protein, 7.46; non-nitrogenous extract, 80.38; crude fat, 0.28; crude fibre, 1.23; and ash, 3.70 per cent. The results of feeding experiments with sheep showed that the food contained 1.5 per cent. of digestible proteids and 71.3 per cent. of digestible carbohydrates. When mixed with cold water, the dried potatoes yield a soft pulp similar to steamed potatoes.

The sheep received as much as 300 grams per day (corresponding with about 1 kilo. of fresh potatoes) without any injurious effects.

N. H. J. M.

Nature of the Nitrogenous Compounds in Soil at Different Depths. GUSTAVE ANDRÉ (*Compt. rend.*, 1902, 135, 1353—1355).—Samples of unmanured soil from the surface and from 30 and 65 cm. below the surface were heated with 3.6 per cent. hydrochloric acid for 15 hours. The soils, which contained respectively 0.166, 0.095, and 0.049 per cent. of nitrogen, yielded, after this treatment, essentially the same proportions of nitrogen in the form of ammonia (about one-seventh). About 12 per cent. of the total nitrogen dissolved in dilute aqueous potash. Similar experiments were made with the soil sampled six months afterwards (in April).

The results indicate that whilst at the end of the summer the nitrogenous matters of the surface soil and subsoil are very similar, in April there is much more soluble nitrogen in the subsoil than at the surface.

N. H. J. M.

Fixation of Ammonia and Potash by Hawaiian Soils. J. T. CRAWLEY and R. A. DUNCAN (*J. Amer. Chem. Soc.*, 1903, 25, 47—50. Compare *ibid.*, 24, 1114).—In order to throw light on the losses of manures when the application is followed by a heavy irrigation, boxes 9 inches square with perforated bottoms were filled with soil to a depth of 1, 2, 4, and 6 inches respectively, manured (10 grams of ammonium or potassium sulphate), and then watered with 4800 c.c. of water.

The following percentage amounts of constituents applied were retained by the different amounts of soil:

Depth of soil (inches).	6.	4.	2.	1.
Ammonia retained per cent. ...	99.84	98.13	86.12	50.21
Potash ,, ,, ...	98.55	94.18	82.03	69.19

Further experiments, in which the 1 inch of soil which received ammonium sulphate was subjected to four more irrigations, showed

that the final amount of ammonia retained was 31·51 per cent. of the total. When the 6 inches of soil manured with potassium sulphate was washed out eight times, it was found that 80·65 per cent. of the total was finally retained.

N. H. J. M.

Tropical Soils. J. D. KOBUS and TH. MARR (*J. Landw.*, 1902, 50, 289—302).—The amounts of the different constituents of Java soils soluble in 2, 4, and 8 per cent. hydrochloric acid and in cold concentrated hydrochloric acid were determined. None of the solvents gave satisfactory results.

It was found that manganese dissolved very readily. Extracts made with very dilute nitric acid yielded amounts of manganese which could be determined, although only traces of iron were dissolved.

N. H. J. M.

Some Cuban Soils of Chemical Interest. WILLIAM FREAR and C. P. BEISTLE (*J. Amer. Chem. Soc.*, 1903, 25, 5—16).—The two Cuban soils and subsoils described are of a deep red colour, only slightly stony and of a calcareous clay nature. Both soils and subsoils have a rather high sp. gr. due to large amounts of iron. The soils contain 2·5 and 2·8 per cent. of organic carbon and 0·255 and 0·230 per cent. of nitrogen; the subsoils, 1·349 and 2·091 per cent. of organic carbon and 0·145 and 0·165 per cent. of nitrogen. Very little sulphur and only traces of chlorine are present. The chief characteristic of the soils is their behaviour towards hot hydrochloric acid, as shown by the following results obtained with the two soils (a) and the subsoils (b):

		Decomposed mineral matter.				
		Insoluble in HCl and in Na ₂ CO ₃ sol.	Gelatinous silica.	Sol. in HCl.	CO ₂ .	Water of combination.
1	{ (a)	7·420	27·080	46·088	0·555	14·599
	{ (b)	15·910	19·820	46·476	0·315	14·482
2	{ (a)	15·930	17·450	46·955	0·275	14·735
	{ (b)	13·050	19·690	48·176	0·305	15·325

The total mineral constituents in the four samples were: K₂O, 0·11—1·90; Na₂O, 0·14—0·22; CaO, 0·22—0·37; MgO, 0·13—0·19; Mn₃O₄, 0·02—0·12; Fe₂O₃, 15·75—17·49; Al₂O₃, 27·86—29·35; P₂O₅, 0·44—0·56; and CO₂, 0·28—0·56 per cent.

N. H. J. M.

Valuation of Basic Slag. B. SJOLLEMA (*J. Landw.*, 1902, 50, 367—370).—Analysis of several samples of basic slag showed that two varieties exist. In the one, the whole of the phosphoric acid dissolves in 2 per cent. citric acid, whilst the amount dissolved by Wagner's method was a good deal (0·8 to 3·0 per cent.) less. The other variety gave both with 2 per cent. citric acid and by Wagner's method still lower results than those obtained with mineral acid. Wagner's method is therefore not to be depended on unless supported by the results of vegetation experiments.

N. H. J. M.

Analytical Chemistry.

New Form of Gas-washing Flask and Absorption Apparatus for Elementary Analysis. J. WETZEL (*Ber.*, 1903, 36, 161—163. Compare Abstr., 1901, ii, 74).—Forms of apparatus are described for use in the absorption of carbon dioxide and water in combustions. The main difference in principle from the ordinary forms is that glass wool, soaked with the absorbing liquid, the potassium hydroxide, or the sulphuric acid, fills the apparatus. The absorption is thus rendered very effective. K. J. P. O.

Siphon Pipette. A. GAWALOWSKI (*Zeit. anal. Chem.*, 1903, 42, 19—20).—The narrow tube below the bulb is bent upwards, and, at a level 2 cm. higher than the mark in the stem, is recurved downwards, the jet being on a level with the lower bend. The pipette is said to be more convenient to use than a straight one. M. J. S.

Estimation of Perchlorates. MAX HÖNIG (*Chem. Zeit.*, 1903, 27, 32—33).—Five to 10 grams of the perchlorate, previously diluted with 20 times its weight of pure potassium nitrate, are fused in a nickel crucible, 2—3 grams of iron powder are added, and the whole is heated for half an hour (not to redness) with frequent stirring. The perchlorate is completely reduced to chloride, which is then estimated gravimetrically with silver as usual.

The process is, of course, applicable to samples of Chili-saltpetre, which often contains a small percentage of potassium perchlorate. Powdered aluminium, zinc, magnesium, and tin have also been tried, but not found to work satisfactorily. L. DE K.

Estimation of Ozone. ALBERT LADENBURG (*Ber.*, 1903, 36, 115—117).—Ozone can be estimated by passing the gas very slowly through a solution of sodium hydrogen sulphite and titrating the unchanged sulphite with iodine. The oxidation of arsenious acid by minute bubbles of ozone gave less satisfactory results; in each case, the weight of the gas was used as an absolute method of determining the proportion of ozone contained in it. T. M. L.

Estimation of the Strength of Sulphuric Acid. ARTHUR MARSHALL (*J. Soc. Chem. Ind.*, 1902, 21, 1511—1512).—A weighed quantity of the concentrated acid is diluted with water until the strength is reduced to 70 or 80 per cent., and the sp. gr. of the mixture taken. The strength of the dilute acid is then ascertained from a table. This, multiplied by the weight of the diluted acid and divided by the weight of the original acid taken, gives the strength of the latter. An allowance for mineral impurities must be made in the case of crude acids. An approximate estimation may also be made by measuring the contraction produced on mixing 200 c.c. of the sulphuric acid with 100 c.c. of water. A table is given showing the contractions for various

strengths of acid; for instance, a 98 per cent. acid contracts 24.1 c.c., whilst an 86 per cent. acid contracts 10.4 c.c. W. P. S.

Examination of Methods employed in estimating the Total Acidity of Gases escaping from the Chamber Process for Manufacture of Sulphuric Acid, with Suggestions arising from the Study of the Interaction of Nitrous and Sulphurous Acids, or their Salts, in Aqueous Solution. R. FORBES CARPENTER and ERNEST LINDER (*J. Soc. Chem. Ind.*, 1902, 21, 1490—1508).—The authors, after a large amount of experimental work, find that hydrogen peroxide in neutral or alkaline solution has no appreciable action on nitrous oxide, but nitric oxide is slowly oxidised to nitrous acid. Nitric oxide is slowly converted into nitric acid by hydrogen peroxide in acid solution. When sulphurous and nitrous acids interact in aqueous solution at 15° and within certain limits of concentration, in the presence of excess of sulphurous acid, reactions proceed according to the three following equations: (a) $2\text{NO}\cdot\text{OH} + 2\text{H}_2\text{SO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$; (b) $\text{NO}_2\text{H} + 2\text{H}_2\text{SO}_3 = \text{OH}\cdot\text{N}(\text{SO}_3\text{H})_2 + \text{H}_2\text{O}$; (c) $\text{OH}\cdot\text{N}(\text{SO}_3\text{H})_2 + \text{H}_2\text{O} = \text{OH}\cdot\text{NH}\cdot\text{SO}_3\text{H} + \text{H}_2\text{SO}_4$. When aqueous solutions of sulphurous and nitrous acids are mixed, the acid recovered by titration is in every case less than the sum of the acidities of the acids taken, whether the titration be performed at once or several days after mixing. Nitric oxide gas is not evolved at any period of the reaction. Tabulated results of works-tests are given. It was found undesirable to rely on sodium hydroxide, or carbonate, alone as an absorbent for the gases from vitriol exits in view of the reactions that may arise with the formation of sulphazotised compounds whose titre is less than that of the constituents separately (compare *Trans.*, 1900, '77, 673).

W. P. S.

Persulphates. N. TARUGI (*Gazzetta*, 1902, 32, ii, 383—392).—A simple and exact method for the estimation of persulphates is based on the transformation they undergo when boiled with water, namely: $\text{M}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{M}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O}$. The initial acidity of the solution of a known weight of the persulphate is first determined; then a known volume is boiled for 20 minutes, cooled, and its acidity determined by titration with standard soda solution, phenolphthalein being the best indicator to use. If, however, ammonium persulphate is to be estimated, the solution is first exactly neutralised by standard soda, of which a known amount in excess is then added; after the boiling, the titration must be made with standard sulphuric acid.

The change produced in a solution of potassium persulphate by heating, namely, $\text{K}_2\text{S}_2\text{O}_8 = \text{K}_2\text{SO}_4 + \text{SO}_3 + \text{O}$, is a unimolecular reaction, which is not interfered with by either the liberation of oxygen or the hydration of the sulphur trioxide. At a temperature of 95°, the mean value for K is 0.0368.

When potassium cyanide and potassium persulphate react in solution in presence of excess of ammonia, 75 per cent. of the cyanide is converted into carbamide, this proportion remaining constant, no matter how the proportions of the two salts are varied. Using a

standard solution of copper sulphate as indicator, the above change can be employed as a means of estimating potassium cyanide, an advantage of the method being that it can be carried out in alkaline solutions. To the cyanide solution are added a known volume of standard copper sulphate solution and excess of ammonia, and into the hot liquid standard persulphate solution is run until a persistent blue colour is obtained; the quantities of cyanide corresponding with the volumes of copper sulphate and persulphate solutions are then added together, the result being 75 per cent. of the total cyanide present.

The black compound formed on mixing solutions of a persulphate and silver nitrate is found to be the silver salt of Caro's persulphuric acid, and is formed according to the equation: $2\text{AgNO}_3 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{Ag}_2\text{SO}_5 + \text{K}_2\text{SO}_5 + \text{HNO}_2 + \text{HNO}_3$.
T. H. P.

Estimation of Ammonia in Urine and Liquids of Animal Origin. OTTO FOLIN (*Zeit. physiol. Chem.*, 1902, 161—176. Compare Abstr., 1901, ii, 575).—The method previously described (*loc. cit.*) does not give good results. The new method consists in adding a feeble alkali, such as sodium carbonate, and removing the ammonia thus produced by the aid of a strong current of air at the ordinary temperature.

Twenty-five c.c. of urine are mixed in a tall cylinder with 8—10 grams of sodium chloride, 5—10 c.c. of light petroleum, and 1 gram of dry sodium carbonate. All the ammonia is removed when a current of air is passed through the liquid for 1—1½ hours at the rate of 600—700 litres per hour at 20—25°. The air is passed over cotton wool and then into two vessels containing *N*/10 acid. A special form of vessel for containing the standard acid is described. J. J. S.

A New Volumetric Method of estimating Hydroxylamine. LOUIS J. SIMON (*Compt. rend.*, 1902, 135, 1339—1342).—The method is based on the action of potassium permanganate on hydroxylamine oxalate in neutral solution. Only the hydroxylamine is oxidised, and the reaction is represented by the equation: $2\text{KMnO}_4 + 4[(\text{NH}_2\cdot\text{OH})_2\cdot\text{H}_2\text{C}_2\text{O}_4] = 2\text{MnC}_2\text{O}_4 + 2\text{KHC}_2\text{O}_4 + \text{N}_2\text{O} + 3\text{N}_2 + 15\text{H}_2\text{O}$. One mol. of permanganate oxidises 4 mols. of hydroxylamine. In presence of sulphuric acid, the oxalic acid is also oxidised.

The oxidation of hydroxylamine sulphate by permanganate takes place according to the equation: $4\text{KMnO}_4 + 5[(\text{NH}_2\cdot\text{OH})_2\cdot\text{H}_2\text{SO}_4] = 4\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 2\text{KNO}_2 + 2\text{N}_2\text{O} + 2\text{N}_2 + 20\text{H}_2\text{O}$; if more sulphuric acid is added, the potassium nitrite is then oxidised. A similar reaction takes place with hydroxylamine hydrochloride.

For the estimation of hydroxylamine in the form of sulphate or hydrochloride, a neutral solution is prepared, and rather more than the molecular quantity of sodium oxalate is added, then the solution is titrated with potassium permanganate. The hydroxylamine behaves as if it were present as oxalate, and its weight is found from $132n\theta/1000$ if *n* c.c. of permanganate containing *θ* grams per litre be used.

Hydroxylamine oxalate may conveniently be used for standardising

permanganate; 50 c.c. of a 1 per cent. solution of hydroxylamine oxalate decolorise 16 c.c. of a *N*/10 solution of potassium permanganate.
J. McC.

Titrimetric Estimation of Nitric Acid. I. ISAAC K. PHELPS (*Amer. J. Sci.*, 1902, [iv], 14, 440—443).—A measured volume of a dilute solution of a nitrate is put into a 250 c.c. flask fitted with a doubly-perforated rubber cork. The inlet tube consists of a 50 c.c. stoppered funnel having its tube constricted at the lower end; its stem is filled with water. The exit tube consists of a glass tube of 0.8 mm. diameter, enlarged just above the cork to a small bulb and bent twice at right angles; during the experiment, the end is made to dip into mercury.

The solution is now boiled until the air has been expelled, and through the funnel is then admitted a definite volume of standardised ferrous sulphate, followed by hydrochloric acid equal in amount to the liquid in the flask. Ferrous ammonium sulphate should not be used. The boiling is continued until 10—15 c.c. of liquid are left; sodium carbonate solution is then introduced so as to neutralise nearly the whole of the acid, and when cold the liquid is titrated as usual with potassium permanganate or with iodine and arsenious acid, and the excess of ferrous iron is thus determined.

When dealing with solid nitrate, this is dissolved in a little water and put into the funnel (the air has been previously expelled from the flask by boiling 10 c.c. of water to a small volume) then adding the ferrous sulphate, and again concentrating to a small volume. After admitting the nitrate, the requisite quantity of acid is run in.

L. DE K.

Estimation of Citrate-soluble Phosphoric Acid. MAX PASSON (*Chem. Zeit.*, 1903, 27, 33).—In order to avoid the trouble caused by the occasional presence of dissolved silica, the author operates as follows: 100 c.c. of the citrate solution are mixed with 10—15 c.c. of sulphuric acid and a drop of mercury, and boiled in a Kjeldahl flask until the contents become clear. While still warm, the residue is diluted with water and a small amount of salt is added to precipitate nearly the whole of the mercury. After diluting to 200 c.c. and filtering, 100 c.c. of the filtrate, now free from silica, are treated as usual with ammonium citrate, ammonia, and magnesium mixture. L. DE K.

Employment of Caro's Acid for the Destruction of Organic Substances [before testing for Arsenic]. N. TARUGI (*Gazzetta*, 1902, 32, ii, 380—382).—In the detection of arsenic in animal tissues, stomach contents, &c., there is difficulty in preventing the volatilisation of arsenic during the destruction of the organic matter. All trouble in this direction is avoided by the following method of treatment. The material to be examined—viscera, muscle, blood—is mixed with an equal weight of powdered potassium percarbonate and half its weight of water and the whole left for 12 hours, after which it is boiled for about half an hour, more percarbonate being added, if necessary, to cause the complete disappearance of fatty matter. The liquid is then carefully decanted from the unattacked material, the

latter being washed with a small quantity of water, which is added to the other liquid, and the whole then evaporated to dryness on the water-bath. Meanwhile, the undestroyed organic matter is mixed with concentrated sulphuric acid and ammonium persulphate (5 times the weight of the original matter of each) and the mixture heated until action begins and the whole mass becomes converted into a transparent liquid; if, on further heating, this liquid turns brown, more ammonium persulphate must be added. This solution is then added, drop by drop, to the dried residue from the percarbonate treatment.

It is found that, if the organic matter subjected to this treatment contained arsenic, the whole of this latter is left in the final liquid, which can be examined by the usual methods. T. H. P.

Estimation of Carbon [in Steel] by Combustion. GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1902, 24, 1206—1210).—A slight modification of Shimer's process. The asbestos containing the carbonaceous residue, obtained in the usual way by treating the sample with copper chloride, is dried for half an hour and placed with the carbon uppermost in a large crucible, and the wad of asbestos used for wiping the funnel is placed to one side; both are then pressed down evenly on the bottom of the crucible by a thick glass rod with a spread-out end. The crucible is now nearly filled with carbon-free, finely-ground copper oxide and then heated for 10 minutes over the blast; during this time, purified oxygen is passed through at the rate of 4 or 5 bubbles per second, and the carbon dioxide is absorbed in a weighed potash apparatus filled with oxygen and containing a lye of sp. gr. 1.4. L. DE K.

Extraction of Carbon Monoxide from Coagulated Blood. MAURICE NICLOUX (*Compt. rend. Soc. Biol.*, 1903, 55, 13—15).—With blood clotted in the ordinary way, the precise determination of the carbon monoxide is not possible: exact results, however, are obtained if the clot is first cut up and then squeezed through linen; the linen is then washed and the washings added before the analysis is made.

W. D. H.

Separation of Quartz and Amorphous Silica. B. SJOLLEMA (*J. Landw.*, 1902, 50, 371—374).—Diethylamine (33 per cent. aqueous solution) was found to dissolve amorphous silica almost completely, and a 16.5 per cent. solution left less than 1 per cent. of the silica undissolved. When 5 per cent. sodium hydroxide solution was employed under similar conditions (boiling for 8 hours), the undissolved residue amounted to more than 2 per cent. Diethylamine (16.5 per cent. solution) dissolved 1.2 per cent. of very finely powdered quartz when boiled for 2 days. As regards other amorphous soil constituents, it was found that 16.5 per cent. aqueous diethylamine dissolved about 15 per cent. of aluminium hydroxide (5 per cent. sodium hydroxide dissolved nearly the whole and 10 per cent. sodium carbonate about 20 per cent.) and about 40 per cent. of aluminium silicate (sodium hydroxide and sodium carbonate dissolved respectively 75 and 20 per cent.). Both substances are completely dissolved by 5 per cent. sodium hydroxide when the solvent is renewed a few times; a

temperature of 60° is sufficient. The results show that von Picdzicki's method for determining free silica in soils (*Mitt. Landw. Inst. Univ. Leipzig*, II, 1, 54) is useless.

N. H. J. M.

Estimation of Free Lime in Basic Slags. M. BISCHOFF (*Chem. Zeit.*, 1903, 27, 33).—Water is recommended for the extraction of basic slags instead of a 10 per cent. sugar solution, as the latter seems also to dissolve calcium hydrogen carbonate and consequently gives erroneous results.

L. DE K.

Separation of Lead from Manganese by Electrolysis. A. F. LINN (*Amer. Chem. J.*, 1903, 29, 82—84).—The following method for the electrolytic separation of lead from manganese gives accurate results. Sodium hydrogen phosphate is added in slight excess to a solution of the nitrates of lead and manganese. The precipitated phosphates are dissolved in excess of phosphoric acid of sp. gr. 1.70 and submitted to electrolysis. The deposit of lead is washed successively with water, alcohol, and ether, and dried at 100—110°. The quantities of lead and manganese should not exceed 0.1 gram for each 130 c.c. of the electrolyte. The time required for this amount is 16—17 hours. If the solution is heated at 60—70°, the deposition of the lead is retarded.

E. G.

Electrolytic Estimation of Mercury and the Solubility of Platinum in Potassium Cyanide. FRITZ GLASER (*Zeit. Elektrochem.*, 1903, 9, 11—17).—The deficit of mercury observed by Bindschedler (*Abstr.*, 1902, ii, 532) is found to be due to a very small extent only to vaporisation of mercury, the main source of error being found in the solubility of the platinum vessel used in the analysis. Solution of the platinum does not occur when mercury is deposited from solutions containing sulphuric acid, potassium sulphate, and hydrocyanic acid or ammonium cyanide, or from solutions containing potassium cyanide when the temperature is low (15—20°) and the current weak. Solution occurs with potassium cyanide solutions at higher temperatures (25—30°) and currents (0.8 ampere on a platinum basin weighing 44 grams). Further experiments show that platinum dissolves in solutions of potassium cyanide in absence of oxygen, giving off hydrogen. The solubility is very small in the cold, but is increased very considerably by rise of temperature or in presence of sodium or potassium amalgam.

T. E.

Volumetric Estimation of Cerium. ANTON WAEGNER and A. MÜLLER (*Ber.*, 1903, 36, 282—284. Compare Knorre, *Abstr.*, 1898, ii, 311).—Bismuth tetroxide is recommended as the oxidising agent in place of persulphuric acid in Knorre's method. The cerium solution is mixed with an equal volume of concentrated nitric acid, and, when cold, bismuth tetroxide (2—2.5 grams for each 0.1 gram of cerium) is gradually added. The solution is made up to a known volume with water, the precipitate allowed to subside, and the solution decanted through a dry filter paper, then diluted with water, and titrated by Knorre's method.

J. J. S.

Quantitative Separations by Persulphates in Acid Solution. MAX DITTRICH and C. HASSEL (*Ber.*, 1903, 36, 284—289. Compare Abstr., 1902, ii, 693, and Knorre, *Zeit. angew. Chem.*, 1901, 14, 1149).—A method is given for the separation of manganese and calcium. The ammonium persulphate is added to the acidified manganese solution in the cold, and the mixture is then gradually warmed on the water-bath; the manganese is thrown down as a deep black, granular precipitate, presumably the dioxide, which can readily be filtered, washed, and ignited and then weighed as Mn_3O_4 . The calcium may be precipitated as oxalate after evaporation of the filtrate.

Manganese and chromium may also be separated by the aid of acidified ammonium persulphate, as the chromium is thus converted into soluble chromates. J. J. S.

Estimation of Manganese in Iron and Steel. JOHN V. R. STEHMAN (*J. Amer. Chem. Soc.*, 1902, 24, 1204—1206).—0.2 gram of the sample is treated in a test-tube with 10 c.c. of nitric acid of sp. gr. 1.2. The tube is placed in boiling water until the iron is dissolved and the liquid is free from nitrous fumes. To the filtrate and acid washings is added 15 c.c. of solution of silver nitrate (1.33 grams per litre), and then 1 gram of ammonium persulphate. After boiling for one minute, the contents are rapidly cooled and transferred to a beaker, the tube is rinsed with about 30 c.c. of water, and 5 c.c. of brine are added. The permanganic acid formed during the process is now titrated with standard solution of sodium arsenite. L. DE K.

Simple Method for Decarbonising Substances. Estimation of Iron, Phosphoric and Hydrochloric Acids in the Decarbonised Product. ALBERT NEUMANN (*Zeit. physiol. Chem.*, 1902, 37, 115—142).—The method consists in heating the organic solid or liquid with a mixture of equal volumes of concentrated nitric and sulphuric acids. The reaction is carried out in a $\frac{1}{2}$ — $\frac{3}{4}$ litre flask, and the mixed acids are slowly run in from a dropping funnel, and the mixture heated during the process until oxides of nitrogen cease to be evolved. The product is then mixed with three times its volume of water and boiled. A modified process is described for urine. The nitrogen in the original substances is not converted into ammonia by this process.

The liquid is rendered slightly alkaline by the addition of ammonia, and the iron precipitated as ferric phosphate, together with zinc ammonium phosphate; under these conditions, the whole of the iron is deposited. The zinc is added in the form of 20 c.c. of a solution containing 25 grams of zinc sulphate, 100 grams of sodium phosphate, and sufficient dilute sulphuric acid to dissolve the precipitate, the whole being made up to 1 litre. The precipitated phosphates of iron and zinc are freed from nitrites, dissolved in dilute hydrochloric acid, the solution rendered just faintly acid, and the iron estimated by the addition of potassium iodide and starch and titration with $N/250$ thio-sulphate at 50—60°. As the dilute $N/250$ thiosulphate solution is very unstable, it is necessary to standardise it repeatedly by the aid of a standard solution of ferric chloride containing free hydrochloric acid.

The phosphoric acid is precipitated as ammonium phosphomolybdate, the precipitate dissolved in excess of $N/2$ alkali, the solution boiled, and the excess of alkali titrated with $N/2$ sulphuric acid, using phenolphthalein as indicator.

Hydrochloric acid is most readily estimated by allowing the gases evolved during decarbonisation to pass over silver nitrate solution. Nitrites are decomposed by boiling with potassium permanganate, the excess of permanganate removed by the aid of ferrous sulphate, and the excess of silver estimated by Volhard's method.

In the estimation of sodium and potassium, it is necessary to heat the undiluted decarbonised solution in a platinum or porcelain dish in order to remove the sulphuric acid. J. J. S.

Iodometry of Ferrous Salts. ERWIN RUPP (*Ber.*, 1903, 36, 164—166).—As is well known, ferric salts can be estimated by titrating the iodine set free from potassium iodide, the reaction being quantitative in the presence of large excess of acid. The reaction $\text{Fe}^{+++} + \text{I}^- \rightleftharpoons \text{Fe}^{++} + \text{I}_2$ is reversible, as ferrous salts will reduce iodine to hydrogen iodide. This reaction is also quantitative in the presence of substances which remove free mineral acid, such as sodium acetate, hydrogen carbonate, or tartrate, but it takes place rather slowly, not being complete (in decinormal solutions) until after 3 hours, although the major part of the iron has been oxidised in 1 hour. The titration is carried out in the following manner: a measured volume, 20—25 c.c., is added to a concentrated solution of 5 grams of sodium potassium tartrate in a glass-stoppered flask and the neutral solution of the ferrous salt run in; after 3 to 5 hours, during which the flask has been kept in the dark, the excess of iodide is titrated by thiosulphate. The method can also be used in order to analyse a mixture of ferrous and ferric salts. In this case, the ferrous salt is first estimated by permanganate, and then potassium iodide added; the total iron now as ferric salt is reduced to the ferrous state, and the iodine set free in the process estimated with thiosulphate. The analyses given show that this method is capable of giving results accurate to 0.5 per cent. K. J. P. O.

Technical Analysis of Ferro-nickel Briquettes. J. H. JAMES and J. M. NISSEN (*J. Soc. Chem. Ind.*, 1903, 22, 3—4).—*Estimation of Copper, Nickel, and Phosphorus.*—One gram of the powdered sample is dissolved in boiling hydrochloric acid, evaporated to a paste, and heated with 5 c.c. of sulphuric acid until fuming commences. The residue is dissolved in 50 c.c. of water, filtered, and the insoluble portion fused with sodium carbonate. The fused mass is treated with dilute sulphuric acid, evaporated, and filtered, the filtrate being added to the main solution. The latter is rendered slightly alkaline with ammonia, just acidified with sulphuric acid, 3 c.c. of nitric acid are added, and the copper is deposited electrolytically. After oxidising the solution from the copper deposit with hydrogen peroxide, the iron is separated from the nickel by precipitation with ammonia, thrice repeated, dissolving the precipitate each time in dilute sulphuric acid. The final precipitate, which contains the phosphorus as ferric phosphate,

is then dissolved in nitric acid and the phosphoric acid estimated by the molybdate method. The first filtrate from the iron separation is evaporated with sulphuric acid, the other filtrates are added, and the whole made strongly ammoniacal. After dilution, the nickel is deposited by electrolysis.

Estimation of Silicon, Aluminium, Calcium, and Magnesium.—Two grams are dissolved in hydrochloric acid and evaporated. The insoluble residue is collected on a filter, fused with sodium carbonate, and the silica obtained from the fusion as usual. The iron and aluminium are precipitated from the combined filtrates with ammonia and filtered. After redissolving the precipitate in dilute sulphuric acid, ammonia is added until a turbidity forms, the latter is dissolved by the addition of a drop or two of dilute sulphuric acid, the solution is diluted to 500 c.c., and the iron electrolytically deposited on 200 grams of mercury placed in the bottom of the beaker. The aluminium is precipitated as usual in the solution decanted from the iron deposit. Calcium and magnesium are precipitated in the filtrate from the iron and aluminium precipitation as oxalate and phosphate respectively, the presence of copper and nickel not interfering, provided that the solution is strongly ammoniacal.

Estimation of Sulphur and Iron.—One gram is fused with a mixture of sodium carbonate and potassium nitrate, the fused mass is dissolved in hot water, and, after filtering, the iron in the residue is dissolved in hydrochloric acid, precipitated with ammonia to remove most of the copper and nickel, and titrated by any of the usual methods. The filtrate is evaporated to dryness and the sulphuric acid precipitated with barium chloride after removing the silica.

Volatile matter.—One gram is heated over the blow-pipe flame, the loss being due to organic matter, water, and practically the whole of the sulphur.
W. P. S.

Detection of Cobalt in presence of Nickel. C. REICHARD (*Zeit. anal. Chem.*, 1903, 42, 10—14).—Cobalt and nickel salts yield basic arsenites ($\text{Co}_7\text{As}_2\text{O}_{10}$ and $\text{Ni}_{14}\text{As}_2\text{O}_{17}$) when their solutions are precipitated with sodium arsenite. If these precipitates are suspended in water and treated with barium peroxide, the nickel compound remains unaltered, whilst the cobalt compound changes from yellow to brown and then to black, in consequence of the formation of cobaltic oxide. On adding potassium cyanide, the nickel salt dissolves, whilst the cobaltic oxide remains insoluble. If, however, the arsenites are first dissolved in potassium cyanide, the solutions give no reaction with barium peroxide. The metals can also be separated without conversion into arsenites. By adding to a solution of cobalt and nickel salts a mixture of barium hydroxide and peroxide, nickel hydroxide and cobaltic oxide are precipitated and can be separated by potassium cyanide.
M. J. S.

Influence of Alkali Tungstates and Molybdates on the Hydrogen Peroxide—Chromic Acid Reaction. C. REICHARD (*Chem. Zeit.*, 1903, 27, 12—13, 27—28).—The results obtained by the author may be summarised as follows: the well-known blue colour appearing on adding hydrogen peroxide to chromic acid is rendered

less delicate and stable by the presence of large amounts of tungstates or molybdates. The reaction is altogether prevented if the tungstate is in excess of the chromate in the proportion of 10 to 1, whilst in the case of molybdate the proportion is as 50 to 1. The reaction is also interfered with by excess of phosphates and arsenates. If these compounds are added after the test has been applied to the pure chromate, the blue colour is at once destroyed. L. DE K.

A Delicate Test for Molybdenum Compounds. LEOPOLD SPIEGEL and TH. A. MAASS (*Ber.*, 1903, 36, 512—513).—A solution of phenylhydrazine in 50 per cent. acetic acid gives a characteristic red coloration when added to very dilute solutions of compounds of molybdenum. It is absolutely necessary to have an excess of phenylhydrazine, and the reaction can be made more delicate by warming the mixture and extracting with a few drops of chloroform, in which the red compound is soluble. 0.00001 gram of molybdenum in 10 c.c. of water can readily be detected by this method. No other substance has been found which answers to the same test. J. J. S.

Electrolytic Estimation of Bismuth and its Separation from other Metals. ALFRED LEWIS KAMMERER (*J. Amer. Chem. Soc.*, 1903, 25, 83—98).—The author finds that under certain conditions it is possible to completely precipitate bismuth by electrolysis in a compact metallic form. The solution should contain in 150 c.c. about 0.1—0.15 gram of bismuth, 1 c.c. of free nitric acid, 2 c.c. of sulphuric acid, and 1 gram of potassium sulphate. The operation, which lasts from 8 to 9 hours, should be conducted at 45—50°. The apparatus used is of the usual description. As cathodes, platinum dishes are used with a surface of 100 sq. cm. The anodes are either flat spirals of two turns of stout platinum wire with an anode surface of 4.5 sq. cm., or basket anodes having a surface of 60 sq. cm. and perforated with a number of holes. The current strength should be from 0.02—0.05 ampere, with a voltage ranging from 1.8—2 volts; towards the end, the current may be raised to 0.15 ampere.

The bismuth may be precipitated in a pure state in the presence of zinc, cadmium, chromium, cobalt, nickel, manganese, uranium, and even iron. For the exact details of the separations, the original article should be consulted. L. DE K.

The Micro-chemical Analysis of Organic Compounds. THEODORE H. BEIHERNS (*Chem. Zeit.*, 1902, 26, 1125—1128, and 1152—1155).—Tests are given for the detection of aliphatic and aromatic aldehydes, hydroxyaldehydes, aldehydic acids, ketones, quinones, ketonic acids, and indigotin by the microscopic examination of the crystals formed when these substances are treated with various reagents, such as phenylhydrazine, potassium ferricyanide and hydrochloric acid, bromine, &c. The appearance and measurement of the crystals are given in each case (compare *Abstr.*, 1902, ii, 634).

W. P. S.

Identification and Composition of Malt Liquors. CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1902, 24, 1170—1178).—The

author has made a large number of analyses of American beers by the usual official processes and tabulated the results. It appears that it is as yet impossible to state with certainty whether malt has been completely omitted in the manufacture of beers. Very valuable data may be obtained from a full analysis of the ash. L. LE K.

Use of Nitrates for the Characterisation of Wines from Sugar. CURTEL (*Compt. rend.*, 1903, 136, 98—100).—Since potassium nitrate, which can readily be recognised in wine by means of diphenylamine, is present in beet sugar, it is suggested that the recognition and estimation of nitrates should be employed in order to ascertain to what extent sugar had been used in the preparation of a wine. K. J. P. O.

Estimation of Essences in Absinths. SANGLÉ-FERRIÈRE and CUNIASSE (*Ann. Chim. anal.*, 1903, 8, 17—18).—100 c.c. of absinth are mixed with 10 c.c. of water and rapidly distilled until 100 c.c. are collected. To 50 c.c. are then added 25 c.c. of a mixture of equal proportions of an alcoholic solution of iodine (50 grams per litre) and an alcoholic solution of mercuric chloride (60 grams per litre). After three hours' action, the excess of iodine is titrated as usual with decinormal solution of sodium thiosulphate. In the meanwhile, a check is made by allowing 25 c.c. of the iodine mixture to act on 50 c.c. of alcohol of the same strength as the absinth.

The difference in c.c. of thiosulphate between the two titrations multiplied by 0.2032 is equal to the grams of essences per litre.

L. DE K.

Estimation of Pentosans. BERNHARD TOLLENS (*Ber.*, 1903, 36, 261—264).—The author has previously (*Abstr.*, 1892, 388, 1433; 1900, i, 244; 1901, ii, 484) drawn attention to most of the points mentioned by Jäger and Unger* (this vol., ii, 187). J. J. S.

Estimation of Starch in Presence of Pentosans. ST. WEISER and A. ZAITSCHEK (*Pflüger's Archiv*, 1902, 93, 88—127). See this vol., ii, 225.

History of Glycogen Analysis. EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 93, 1—19, 20—23).—Polemical. A reply to E. Salkowski (*Abstr.*, 1902, ii, 47), who has stated that Lebbin had precipitated glycogen from alkaline solutions by means of alcohol before the author had used this process. The latter shows that the method is an old one and was in use by Claude Bernard as early as the year 1857. The second paper is a reply to Lebbin (*Abstr.*, 1899, ii, 256). W. P. S.

Action of Dilute Potassium Hydroxide on Glycogen at 100°. EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 93, 77—97).—Further experiments on the action of a boiling 2 per cent. solution of potassium hydroxide on glycogen (compare *Abstr.*, 1902, ii, 586). The results show that the latter undergoes slight decomposition whether it be precipitated by alcohol before inversion or not. With

glycogen prepared by the Brücke-Külz method, the action is more pronounced.
W. P. S.

Estimation of Glycogen. EDUARD PFLÜGER (*Pflüger's Archiv*, 1902, 93, 163—185).—One hundred grams of finely divided flesh are heated on the water-bath with 100 c.c. of 60 per cent. potassium hydroxide solution. After 15 minutes, the flask containing the mixture is closed by an india-rubber stopper and the heating continued for 2 hours. The contents, when cold, are diluted with water to 400 c.c. and filtered through asbestos. One hundred c.c. of the filtrate are precipitated with 100 c.c. of alcohol of 96 per cent. and left for 12 hours. The precipitate is collected on a filter, washed with a mixture of 1 volume of 15 per cent. potassium hydroxide solution and 2 volumes of alcohol, then with alcohol alone, and finally dissolved in cold boiled water. The solution is neutralised with hydrochloric acid, diluted to 500 c.c. after the further addition of 25 c.c. of hydrochloric acid, and inverted by heating on the water-bath for 3 hours. The copper reducing power of the solution is then taken and the quantity of glycogen calculated by reference to tables given. Much detail is given in the original paper, the principle of each step in the process being demonstrated.
W. P. S.

Titration of Fatty Acids of High Molecular Weight. ARISTIDES KANITZ (*Ber.*, 1903, 36, 400—404).—Owing to the hydrolytic dissociation of the soaps of the higher fatty acids, the titration of these acids by means of *N*/10 sodium hydroxide, using phenolphthalein as indicator, gives correct results only in strongly alcoholic solutions; for oleic, palmitic, and stearic acids, the amount of alcohol present has to exceed 40 per cent. of the volume of the solution. A similar quantity of methyl alcohol is necessary, but 10 per cent. of amyl alcohol is sufficient to completely prevent hydrolysis.
W. A. D.

Detection of Ordinary Tartaric Acid by means of *l*-Tartaric Acid. J. N. BRÖNSTED (*Zeit. anal. Chem.*, 1903, 42, 15—19).—Solutions containing less than 0.1 per cent. of *d*-tartaric acid give no precipitate with calcium acetate, but on adding a few drops of *l*-tartaric acid or its ammonium salt a precipitate of calcium racemate is obtained, even from solutions as dilute as 0.0001 per cent. Similarly, the sensitiveness of the calcium test for *l*-tartaric acid is increased by adding *d*-tartaric acid. Calcium can even be estimated with accuracy by precipitating it from a cold acetic acid solution with ammonium racemate.
M. J. S.

Estimation of Salicylic Acid. SIDNEY HARVEY (*Analyst*, 1903, 28, 2—4).—The article of food, wine, or other substance containing salicylic acid is extracted with ether, the ethereal solution being in turn shaken with two successive volumes of water containing a little sodium hydroxide. After carefully neutralising the aqueous extract, it is diluted to 250 c.c. To a known volume, 1 or 2 c.c. of a 1 per cent.

solution of iron-alum are added, and the coloration produced compared with that given by a known quantity of salicylic acid. One part of the latter in 3,000,000 parts of water can be detected. The solution of iron-alum keeps well if a drop or two of sulphuric acid per 100 c.c. be added.

W. P. S.

Influence of Different Proteids on Fats. F. PASTROVICH and FERDINAND ULZER (*Ber.*, 1903, 36, 209—211).—Specimens of oleomargarine have been mixed with different proteids; for example, globulin, serum-albumin, albumose, alkali-albumin, acid-albumin, and casein, and the acid numbers determined at the end of 1, 2, 4, 6, 10, and 14 weeks. In some cases, 1 per cent. of water was also added. The results prove that the presence of the proteid alone affects the acid number but very slightly, whether kept in the dark or exposed to diffused daylight. The presence of water together with a proteid, especially casein, increases the acid number to a considerable degree.

J. J. S.

Refraction of Butter Fat. ED. BAIER (*Zeit. Nahr. Genussm.*, 1902, 5, 1145—1150).—The refractometer numbers of butters produced in winter (November to May) showed less variation than those of summer butters. At a temperature of 35°, 57 per cent. of the winter butters had a refractometer number of 45, 26 per cent. indicated 44, and of the remainder, only 5 per cent. gave a reading as high as 46.9. Summer butters gave wider readings; 93 per cent. had numbers between 46 and 48, and the remainder from 44 to 45.

A thermometer for use in the refractometer is also described. Instead of the ordinary temperature degrees, the scale is marked in refractometer numbers. On one side of the mercury column, the summer scale is given, and, on the other side, the winter scale, the latter numbers being less by 2 than the former.

W. P. S.

Calculation of the extent of Skimming and Diluting in the Analysis of Milk. ÉMILE LOUISE and CH. RIQUIER (*Compt. rend.*, 1903, 136, 122—123. Compare *Abstr.*, 1901, ii, 429).—A criticism of Génin's method of calculation (*Abstr.*, 1902, ii, 183), in which the diminution in volume due to skimming is not taken into account.

N. H. J. M.

Halphen's Test for Cotton-seed Oil. ELTON FULMER (*J. Amer. Chem. Soc.*, 1902, 24, 1148—1155).—The author's experiments show that cotton-seed oil is rendered inactive towards Halphen's sulphur test by heating it at 260—270°, and the delicacy of the reaction is already much diminished by heating at 220—240°. Halphen's reaction is therefore not a trustworthy test for the complete absence of cotton-seed oil. Heating at 220—240° does not render the oil inedible, and even a temperature of 280° might, possibly, not injure its qualities.

Lard from pigs fed on cotton-seed meal gives a decided reaction for cotton-seed oil.

L. DE K.

The Iodine Absorption Number of Cod Liver Oil. J. J. A. WIJS (*Zeit. Nahr. Genussm.*, 1902, 5, 1193—1196).—Twenty-one samples of medicinal cod liver oil gave numbers from 164.2 to 174.7, as estimated by the author's iodine monochloride method. Thirty-nine other oils, crude and refined, obtained directly from the factories in Bergen had iodine numbers varying from 154.5 to 181.3. The Hübl numbers were from 6 to 10 per cent. lower. W. P. S.

Application of Kreiss's Reaction to Preparations of Almonds. A. CHWOLLES (*Chem. Zeit.*, 1903, 27, 33—34).—The author states that almond oil does not give Kreiss's reaction (this vol., ii, 114), and that by this test the presence of peach-kernel oil may be safely detected.

The sweet known as marchpane, a mixture of ground almonds and sugar, is said to be frequently adulterated with ground peach-kernels. By extracting the oil and applying the test, this fraud may be detected. L. DE K.

Estimation of Caffeine. F. KATZ (*Chem. Centr.*, 1902, i, 1526—1527; from *Ber. Deutsch. pharm. Ges.*, 12, 250—257).—Ten grams of the powdered material are shaken for half an hour with 200 grams of chloroform and 5 grams of ammonia. One hundred and fifty grams of the filtrate are distilled to dryness, the residue is dissolved in 5 c.c. of ether and mixed with 20 c.c. of 0.5 per cent. hydrochloric acid; when dealing with coffee beans, 0.2—0.5 gram of paraffin wax is also added. The ether is expelled by evaporation, and the aqueous liquid is filtered and repeatedly extracted with chloroform. The united chloroform solutions are filtered and distilled to dryness; the residual caffeine is then dried on the water-bath and weighed.

When the process is applied to Paraguay tea, the alkaloid obtained is not quite pure. After expelling the ether from the acid liquid, the latter should be mixed with 2 c.c. of an emulsion of lead hydroxide (1:20) and heated for 10 minutes on the water-bath. After adding a few decigrams of magnesium oxide, the liquid is filtered and extracted with chloroform. When testing roasted coffee, 0.2—0.5 gram of paraffin wax should also be added, or else the lead emulsion should be increased to 6—8 c.c.

Tinctures are freed from alcohol by evaporation, and the residue treated with ammonia and chloroform as directed. L. DE K.

Estimation of Theobromine in Cocoa. PAUL WELMANS (*Chem. Centr.*, 1902, ii, 1395; from *Pharm. Zeit.*, 47, 858).—A modification of Decker's method. Five grams of the powdered cocoa, or 10 grams of chocolate, are boiled in a reflux apparatus for an hour with 5 grams of magnesium oxide and 300 c.c. of water. After being kept for another hour in a boiling water-bath, the supernatant liquid is decanted on to an asbestos filter and the residue is washed twice by

decantation with 200 c.c. of boiling water before being collected on the filter. After applying suction, the contents of the filter are mixed with 2 grams of magnesium oxide, and the boiling operation is repeated. The united filtrates and washings are evaporated to dryness with addition of sand, the residue is powdered and boiled 3 or 4 times in succession for half an hour with 100 c.c. of chloroform. The residue from the chloroform is dissolved in a 10 per cent. ammonia, and the filtrate is evaporated to dryness in a weighed platinum dish. The residue is finally dried for half an hour at 100° and weighed. Any ash is allowed for.

L. DE K.

Approximate Estimation of the Bitter Principle and Aroma of Hops. THEODOR REMY (*Chem. Centr.*, 1902, ii, 1279; from *Woch. Brauerei*, 19, 614—618).—The author has attempted to separate the total bitter principles of an acid nature existing in hops (Abstr., 1900, ii, 746, and 1901, i, 40) from each other, the different solubilities of the lead salts being employed for this purpose. It was found that there was a certain relation between the amounts of α -acid and β -acid, the former predominating in the more bitter samples of hops. The manuring appeared to have no influence on the proportions of these acid substances. Further experiments on the estimation of mustard oil in hops showed that the actual presence of this oil was doubtful.

W. P. S.

New Method of Detecting Turmeric. ALBERT E. BELL (*Pharm J.*, 1902, [iv], 15, 551).—The following method is recommended for the detection of turmeric in complex powders such as those of rhubarb and mustard. The reagent used consists of a solution of diphenylamine (1 gram) dissolved in a mixture of 90 per cent. alcohol (20 c.c.) and sulphuric acid (25 c.c.). A drop of this solution is placed on a slide, a small quantity of the powder is spread evenly on a cover-glass and carefully dropped into the reagent on the slide. The slide is then examined with the microscope, and if turmeric is present spots of a fine purple colour are observed; by the number of these spots, the amount of turmeric in the powder can be approximately estimated. E. G.

Detection of Corn-Cockle and Ergot in Flour. LUDWIG MEDICUS and H. KOBER (*Zeit. Nahr. Genussm.*, 1902, 5, 1077—1091).—Corn-cockle (*Agrostemma Githago*) in flour is most readily detected by extracting the latter, after removal of fat with light petroleum, with a mixture of 80 grams of chloroform and 20 grams of alcohol. The residue left on evaporating the solvent gives a brownish-red coloration with concentrated sulphuric acid should corn-cockle be present. The extract from pure wheat meal remains colourless. The authors agree with Kruskal that agrostemmine is not a definite alkaloid, but that it contains sapotoxin and choline. Ergot is best detected by means of Hoffmann's reaction. Ten grams of the flour are shaken from time to time for 6 hours with 20 c.c. of ether and 10 drops of sulphuric acid (1:5). The ethereal extract, on agitation with 10 drops of a cold saturated solution of sodium hydrogen carbonate, gives a violet coloration in the presence of ergot. This coloration, however, is

also given by the colouring matters contained in corn-cockle. Two colouring matters have been isolated from the latter, similar to the sklererythin and skleriodin of ergot.

W. P. S.

Toxicological Detection of Blood. WILLIAM KÜSTER (*Zeit. angew. Chem.*, 1902, 15, 1317—1323).—A report of a lecture on the detection of human blood spots. Particular value is attached to the serum test (compare *Abstr.*, 1902, ii, 635). It is remarked that blood of monkeys also gives a precipitate with the serum of the injected rabbits.

L. DE K.

A Simple Method for the Estimation of Albuminous Substances in Blood. ADOLF JOLLES (*Chem. Centr.*, 1902, ii, 1224; from *Münch. med. Woch.*, 49, [38]).—0.2 c.c. of blood is gently boiled with about 120 c.c. of water and 1 c.c. of sulphuric acid of sp. gr. 1.84, and oxidised by the addition of 10—15 c.c. of 8 per cent. potassium permanganate solution. After removal of the precipitated manganese dioxide by means of oxalic acid, the solution is evaporated to a bulk of 25 c.c., cooled, and neutralised. The nitrogen in the solution is then estimated in a nitrometer similar to Knop-Wagner's instrument. On multiplying the weight of nitrogen found by 7.76, the albumin is obtained. Experiments show that the results agree sufficiently for clinical purposes with those obtained by Kjeldahl's method.

W. P. S.

Colour Reaction of Tyrosine. CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1902, 37, 86—87).—If tyrosine is added to a reagent consisting of formalin 1, distilled water 45, and concentrated sulphuric acid 55 parts, a green coloration is developed on boiling. The test gave negative results when tried with 100 other substances allied to tyrosine.

W. D. H.

Organic Arsenic in Therapeutics. Cacodylic and Methylarsinic Acids and their Salts. LUIGI D'EMILIO, jun. (*Chem. Centr.*, 1902, ii, 1277; from *Boll. Chim. Farm.*, 41, 633—639).—A synopsis is given of the therapeutical uses of arsenic and the application of cacodylic and methylarsinic acids as preventives of malaria. For the estimation of the arsenic in cacodylic acid and its salts, from 0.2—0.25 gram of the substance is heated with 5 c.c. of concentrated sulphuric acid and 1 gram of potassium sulphate. It is necessary to add potassium permanganate to insure complete destruction of the organic matter, heating with sulphuric acid alone not being sufficient. The acid solution is then diluted with water, ammonia is added until the reaction is only feebly acid, and the arsenic is precipitated with hydrogen sulphide. The arsenic trisulphide formed is extracted with benzene to remove free sulphur, dried at 100°, and weighed.

W. P. S.

General and Physical Chemistry

Existence of a Relationship between the Spectra of some Elements and the Squares of their Atomic Weights. W. MARSHAL WATTS (*Phil. Mag.*, 1903, [vi], 5, 203—207).—Two distinct kinds of connection between the spectra of allied elements appear to exist. In the first, the differences between the oscillation frequencies of certain lines of one element are to the differences between the frequencies of the corresponding lines of the second element in the same ratio as the squares of the atomic weights. This is the case in the zinc, cadmium, and mercury family. In the second class, the element of greater atomic weight has the smaller frequency, and if a corresponding line in the spectrum of three elements be compared, the differences of frequency are proportional to the differences between the squares of the atomic weights. In the first case, the atomic weight of one element can be calculated from that of the other element; in the second case, from those of the two others, if the correspondence of the lines be assumed. Thus, from the frequencies of 24 lines in the spectra of zinc and cadmium, values ranging from 64.69 to 65.69 are obtained for the atomic weight of zinc. From the atomic weight of mercury, 119.71, values ranging from 110 to 113 are obtained for the atomic weight of cadmium. In the second class, values from 87.2 to 87.8 are obtained for the atomic weight of strontium, those of barium and calcium being known. Similarly, by comparison of the line of caesium, rubidium, and potassium, values varying from 83 to 86.8 are obtained for the atomic weight of rubidium.

L. M. J.

Spectra of Hydrogen and Reversed Lines in the Spectra of Gases. JOHN TROWBRIDGE (*Phil. Mag.*, 1903, [vi], 5, 153—155).—Employing a quartz tube filled with hydrogen, and a potential difference of twenty thousand volts, the author obtains a most intense, dazzling white light with a blue tint. The spectrum appears continuous, and photography fails to reveal bright lines between the HH lines and the red end. In the region, however, beyond the limit set by the absorption of the glass, bright and dark lines occur. The chief reversed lines are 2889.7, 2549.89, 2528.60, 2524.29, 2519.3, and 2516.21, and correspond with the lines of silicon. The author considers that the presence of dark lines in the spectra of stars does not necessarily imply the presence of reversing layers of a colder state of the gases, as the reversal may arise from photographic action on the plates, for his experiments indicate that the reversal of a metallic line occurs when it falls on a bright gaseous line or band (*Abstr.*, 1902, ii, 589).

L. M. J.

Spectrophotometric Study of some Electrolytes in Solution. P. VAILLANT (*Ann. Chim. Phys.*, 1903, [vii], 28, 213—282).—An

historical account is given of the work of Ostwald, Magnanini, Wagner, Donnan, Ewan, Spring, and others on the colours of solutions as interpreted by the theory of electrolytic dissociation. By means of a Gouy spectrometer, the absorption coefficient for light of definite wave-length was determined for solutions of several salts. The concentrations of the solutions were ascertained by determining the conductivity. Solutions of permanganates of potassium, barium, and zinc were examined; in very dilute solution, these have the same absorption, and the colour varies somewhat with the concentration. The effect of the addition of an electrolyte with the same cation was also investigated. Solutions of copper nitrate in water, alcohol, and a mixture of these were examined; cupric sulphate in water, methyl alcohol, glycerol, methyl alcohol and glycerol, and water and glycerol were also studied. In methyl alcohol and in glycerol, the copper is dissolved as $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$, and the green copper sulphate hydrate is $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. Cupric acetate was studied in alcoholic, aqueous, and acetic acid solution; the addition of acetic acid to the aqueous solution changes the colour from blue to green, although the degree of electrolytic dissociation is but slightly altered. Cupric chloride and bromide were likewise examined in aqueous and alcoholic solutions, and the effect of adding soluble chlorides and bromides to these solutions was observed. When much of another chloride is added to a dilute solution of cupric chloride, the colour changes from blue to green, and the same change is caused by the addition of a small quantity of the other chloride to a more concentrated solution of the copper salt. Cupric bromide appears to exist in the green tetrahydrate form and in the brown, anhydrous condition in solution.

Cobalt nitrate and chloride were examined in aqueous and alcoholic solutions. In aqueous solution, the nitrate exists as hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and the addition of another nitrate causes a change in the degree of dissociation, but not in the state of hydration, and this is accompanied by an alteration of the absorption. Cobalt chloride in dilute solution has a red colour, due to the dissolved hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, but as the concentration increases the blue dihydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, is produced, and there is a consequent change in the absorption. The addition of acetic acid or hydrochloric acid causes a similar change, and the latter acid may, by its presence, give rise to a less hydrated salt than $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$.

The results obtained indicate that the ion possesses its own colour independently of the molecule, and the addition of a colourless electrolyte may modify the colour of a solution containing an electrolyte with a coloured ion both by changing the dissociation and by causing dehydration. These two actions are independent of each other, and the latter depends on the tendency of the added electrolyte to form hydrates. In pure organic solvents, the molecule is in a definite state of hydration, which is generally lower than that in which it exists in aqueous solution. The organic solvent, like an added electrolyte, exerts a dehydrating action. The results are best interpreted in favour of the theory of ionisation, although hydration certainly plays a part; but the hydrate theory is insufficient to explain the observed phenomena.

J. McC.

Excited Radioactivity and the Method of its Transmission. E. RUTHERFORD (*Phil. Mag.*, 1903, [vi], 5, 95—117).—Thorium and radium give off radioactive emanations which behave like radioactive gases or vapours, but the emanation from thorium loses its radiating power far more rapidly than that from radium. It is the emanation which has the power of producing radioactivity in other bodies. This excited radioactivity appears to be due to positively-charged carriers, and experiments were made to determine their velocity in an electric field, and hence to estimate approximately their magnitude compared with that of a gaseous ion. It was found that at 18°, in dry air, the average velocity, in the case of the excited radioactivity from thorium emanations, was about 1.3 cm. per sec. for a potential gradient of 1 volt per cm., that is, a velocity very nearly equal to that of the positive ion produced by the Röntgen or Becquerel rays. The velocity is probably also very nearly equal to this in the case of the radioactivity induced by the radium emanations. It was found that if a plate was exposed for a short time to thorium emanations and then removed, it gradually increased in radioactive power for several hours. The origin and nature of the emanation and of the carrier is discussed. It is considered most probable that the emanation consists of unchanged particles which produce positively-charged carriers by the expulsion of a negatively-charged substance of some kind. The author considers this more probable than the condensation of positive ions on these particles, as the emanation is not removed more rapidly by increasing the number of ions in the gas. The radioactivity is probably the accompaniment and result of a succession of chemical changes occurring in the radioactive matter, changes most probably complex in character.

L. M. J.

Induced Radioactivity and the Emanation of Radium. PIERRE CURIE (*Compt. rend.*, 1903, 136, 223—226. Compare this vol., ii, 50).—It has been previously shown that the rate of decrease of induced radioactivity is given by the exponential expression, $I = I_0 e^{-t/\theta}$ (*loc. cit.*); experimental evidence is now brought forward which shows that the constant, θ , to which was assigned the value 4.97×10^5 seconds, keeps this value between the limits of temperature, -180° and $+450^\circ$. Rutherford's view (this vol., ii, 123), that induced radioactivity depends on a material emanation, appears to the author unnecessary, and is, further, in opposition to the fact that the rate of decrease is independent of the temperature and of other conditions which affect chemical transformations. According to the author, the emanations of radium are not material, but a characteristic form of energy which may appear to be carried by a gas, because the molecules of the gas afford centres of condensation for the energy. In the case of solid salts of radium, the special emanation as it arises is changed into Becquerel rays, but in the solutions of the salts of radium this special emanation goes further afield, and can cause induced radioactivity on the walls of the confining vessel.

K. J. P. O.

Disappearance of Radioactivity Induced on Solid Substances by the Action of Radium. PIERRE CURIE and J. DANNE (*Compt. rend.*, 1903, 136, 364—366. Compare this vol., ii, 50, and preceding

abstract).—All solid substances become radioactive under the influence of the emanation from radium in a closed space, and slowly lose this property when the influence is withdrawn. Provided that the substance has been exposed to the radium for more than 24 hours, the law of the disappearance of the radioactivity is independent of the nature of the substance. The disappearance of activity follows an exponential law, $I = I_0 e^{-t/\theta_1}$, where I is the intensity of radiation after a given time, t , and θ_1 a constant of the value, 2400 seconds. The activity has diminished by half its value in 28 minutes; the radioactive energy disappears more rapidly when it is found on an active solid substance than when it is in the form of an emanation. In the latter case, it diminished by a half in four days (*loc. cit.*).

When the exposure to radium has extended over a less period than 24 hours, the intensity of radiation sinks at first rapidly, then rises to a maximum, and finally decreases regularly. The induction of the radioactivity under the influence of radium follows, up to a limiting value, the same law as the disappearance of radioactivity. A substance on which radioactivity has been induced can, in its turn, induce activity on other substances.

Experiments have been made with such different substances as aluminium, copper, lead, bismuth, platinum, silver, glass, alum, and paraffin, which all behave in the same manner. Cellulose and india-rubber, on the other hand, are peculiar; after a certain time, the rate of disappearance of radioactivity decreases and finally becomes very slow.

K. J. P. O.

Magnetic and Electric Deviation of the easily absorbed Rays from Radium. E. RUTHERFORD (*Phil. Mag.*, 1903, [vi], 5, 177—187).—Hitherto, the α -rays emitted from radium have been regarded as not deviable by a magnetic field. The author, however, using an exceedingly active sample of radium in a field of 8370 C.G.S. units, has obtained deviation of these rays. The amount deviated is approximately proportional to the field, and the deviation is very slight compared with that of the cathode rays, for whereas under the experimental conditions cathode rays would have described an arc of about 0.01 cm. radius, the arc described by the α -rays had a radius of about 39 cm. The direction of deviation is opposite to that of the cathode rays, and the α -rays, therefore, consist of positively charged particles. Deviation was also obtained in an electric field. The author calculates that the value of $H\rho$, where H is the strength of the field and ρ the radius of curvature of the path of the rays, is about 390,000, and the velocity of the rays is hence about 2.5×10^9 cm. per sec., whilst the ratio of the charge to the mass of the carrier is approximately 6×10^3 .

L. M. J.

Magnetic Deviation and Nature of certain Radiationsemitted by Radium and Polonium. HENRI BECQUEREL (*Compt. rend.*, 1903, 136, 199—203).—Rutherford (*Abstr.*, 1902, ii, 637, and preceding abstract) has recently shown that some of the so-called non-deviable radiations of radium have a small deviability when under the influence of a very strong magnetic field, and are therefore analogous to Gold-

stein's "canal rays." With the aid of a photographic method, the author has reinvestigated this point, and has confirmed Rutherford's observations. It would seem that the α -radiations of radium carry positive charges, having greater masses and less velocity than the cathode rays, and thus resemble the "canal rays."

Owing to the method not giving such decisive results in the case of polonium, the evidence of the deviability of the radiations is not so strong, but a small deviability (of the same order of magnitude as in the case of radium) appears to exist.

K. J. P. O.

The Radiation from Polonium and from Radium. HENRI BECQUEREL (*Compt. rend.*, 1903, 136, 431—434).—It has already been proved (preceding abstract) that the α -rays from radium are identical with the polonium rays, and appear also to be the same as Goldstein's "canal rays." Further proof of this has been found by projecting the rays deviated in the magnetic field on to a photographic plate; the impressions produced, using polonium and radium, are superposable. The radium rays are much more intense than those from polonium. The impressions on the plate are in the form of fine lines and give no indication of dispersion, even when a very intense magnetic field was applied.

A similar method has been used to study the mode of propagation of the very deviable part of the radium radiation through transparent substances. The least deviated rays can pass through an aluminium plate 0.1 mm. thick without alteration; the more deviated rays can also traverse this, but on emerging give rise to secondary rays. The most deviated rays are arrested by a very small thickness of material, and they provoke secondary rays at the incident face. In their propagation through paraffin, the deviated rays maintain their curvature. The more deviated the ray is, the less is it able to penetrate.

J. McC.

Induced Radioactivity caused by Salts of Actinium. A. DEBIERNE (*Compt. rend.*, 1903, 136, 446—448).—When substances are placed in a closed vessel along with an actinium compound, they become radioactive. The induced activity is not uniform like that induced by radium salts, but more intense in that part of the substance nearest the source of excitation. Gas in contact with actinium preparations also becomes intensely active; the radioactivity of actinium salts can be greatly decreased by passing a current of air over them. When a substance is placed in a vacuum along with an actinium salt, it becomes uniformly radioactive. The intensity of the induced activity is dependent on the volume of the free space in the enclosing vessel. The activity induced by actinium salts is lost much more slowly than that induced by radium. The time taken for induced activity to diminish to half its intensity may serve as a guide as to whether the activity has been induced by radium, thorium, or actinium salts. The author discusses Curie's hypothesis of centres of actuating energy which produce the induced activity, and these are the same as Rutherford's emanations. The results of some experiments lead the author to believe that these actuating centres emit a radiation which

is the cause of the excitation, and these rays, like the cathode rays, are deviated in a magnetic field.

J. McC.

Absorption of Gravitation Energy by Radioactive Matter. ROBERT GEIGEL (*Ann. Physik*, 1903, [iv], 10, 429—435).—A small lead ball was suspended from one arm of an accurate balance, and counterpoised. If a watch-glass with a layer of radioactive material was suspended below the lead ball, the latter, as shown by the altered swing of the pointer, became apparently lighter, the loss of weight being 0.05—0.2 mg. on a total weight of 6.5 grams, according to the thickness of the layer of radioactive material. This loss of weight is attributed by the author, not to any electrostatic repulsion or to the impacts on the ball of particles emanating from the radioactive material, but to the absorption of gravitation energy by the latter.

J. C. P.

Cadmium Amalgams. WILHELM JAEGER (*Zeit. physikal. Chem.*, 1903, 42, 632—633).—In reference to Bijl's paper (this vol., ii, 6), the author points out that he has all along admitted the instability under certain conditions of a Weston cell containing a 14.3 per cent. cadmium amalgam. All difficulties are avoided, however, by the use of an amalgam containing 12 or 13 per cent. of cadmium (compare also von Steinwehr, this vol., ii, 147).

J. C. P.

The Potential Difference which Occurs at the Surface of Contact of Two Different Non-miscible Liquids in which a Dissolved Electrolyte has Distributed Itself. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 431—437).—A theoretical paper not suitable for abstraction.

A. McK.

Steady Current ("Reststrom") in Galvanic Polarisation Regarded as a Diffusion Problem. F. G. COTTRELL (*Zeit. physikal. Chem.*, 1903, 42, 385—431).—A physical paper. When an external *E.M.F.* is applied to a cell of the type $\text{Ag} | \text{AgNO}_3 | \text{Ag}$, there is a change of concentration at the electrodes; consequently, diffusion sets in, tending to restore equality of concentration. In order, therefore, to maintain the difference of concentration at the electrodes, a steady current must be sent through the cell. It is the relation between this steady current and the process of diffusion that the author treats theoretically and experimentally. The theory developed is confirmed by the experiments. It is shown that the method employed may be made a basis of the determination of diffusion constants. A method is given for finding the rate of migration of certain ions in a large excess of other electrolytes.

J. C. P.

A Law relating to the Electromotive Force of Voltaic Elements Based on the Reciprocal Action of Salt Solutions and Soluble Electrolytes. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 136, 413—426).—The *E.M.F.*, which can be obtained by the neutralisation of an acid by a base, is found to be equal to the sum of the *E.M.F.* developed by the action of the corresponding salt on the

acid on the one hand, and on the base on the other. The solutions are supposed to be dilute and isotonic, and no change other than neutralisation is supposed to take place. This law has been experimentally verified in the case of sodium hydroxide and the following acids: sulphuric, hydrochloric, nitric, boric, formic, acetic, and oxalic, and with ammonia and sulphuric and hydrochloric acids. In all cases, the *E.M.F.* of acid | base was found to equal to the sum of the *E.M.F.* of salt | acid and base | salt when non-polarisable electrodes were used. In the case of the organic acids, the agreement was not so good, but the divergence can be attributed to polarisation. The energy required for the production of a continuous *E.M.F.* in the reaction of an acid on a base can be traced to a chemical origin. The *E.M.F.* of which this is the sum appear to derive their energy from some source external to the system, and this seems to be the development of electrolytic dissociation.

J. McC.

Law of the Electromotive Forces of Salt Solutions: Influence of Temperature. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 136, 481—485).—The results previously found at 12° or 14° indicate that the *E.M.F.* developed by the action of an acid on a base is equal to the sum of the *E.M.F.* of the acid on the salt and of the base on the salt (this vol., ii, 125). In precisely the same manner, this has now been proved to be true at 51°.

The *E.M.F.* developed by the action of an acid on a base increases with the temperature; this increase is correlative with the increase of the *E.M.F.* developed by the action of acid on salt, whilst that due to the action of base on salt seems not to vary with temperature.

It has further been proved that the law applies also to more concentrated solutions than those formerly used.

J. McC.

Range of Validity and Constancy of Faraday's Law. THEODORE W. RICHARDS and WILFRED NEWSOME STULL (*Zeit. physikal. Chem.*, 1903, 42, 621—625. Compare Richards, Collins, and Heimrod, *Abstr.*, 1900, ii, 256; Richards and Heimrod, *Abstr.*, 1902, ii, 592).—When a current is passed (1) through an aqueous solution of silver nitrate at 20°, (2) through a solution of silver nitrate in fused sodium and potassium nitrates at 250°, the two solutions being in series, the amounts of silver deposited in the two cases are the same to within 0.005 per cent. These experiments prove that the validity of Faraday's law is independent of the temperature and of the nature of the solvent (compare Helfenstein, *Abstr.*, 1900, ii, 383; Kahlenberg, *Abstr.*, 1900, ii, 521).

J. C. P.

Equivalent Conductivity of the Hydrogen Ion Derived from Transference Experiments with Hydrochloric Acid. II. ALBERT A. NOYES (*J. Amer. Chem. Soc.*, 1903, 25, 165—168).—The transport numbers of 1/60 molar hydrochloric acid at 10°, 20°, and 30° have been determined by A. A. Noyes and Sammet (this vol., ii, 126); the conductivity of the chlorine ion being known, it was possible to deduce that of the hydrogen ion. The values so obtained were 4 to 6 per cent. higher than those of Ostwald and Kohlrausch deduced

by a different method. To find out whether this variation was due to a difference in the transport numbers of the acid at extreme dilution and at the investigated dilution of 60 litres, a new set of determinations with a 1/180 molar hydrochloric acid at 20° was carried out.

The conclusion is drawn that the transport number of hydrochloric acid does not appreciably change with increase of the dilution after 60 litres.

A. McK.

Saturated Gypsum Solutions as a Basis for Conductivity
 GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1903, 42, 577—583).—The author has shown (Abstr., 1901, ii, 493) that the concentration of a saturated calcium sulphate solution may vary as much as 20 per cent., according to the size of the particles of the solid salt with which it is in contact; it is, therefore, very necessary, in using a saturated gypsum solution as a standard electrolytic resistance, to see that the saturation is normal (compare Hulett and Allen, Abstr., 1902, ii, 656). This is best secured by taking clear gypsum crystals, free from chloirine, splitting them into thin laminæ, and shaking the latter with pure water for several hours. The conductivities of saturated solutions obtained in this way at various temperatures between 10° and 30° are given below:

Temp.	Spec. conductivity (λ).
10°	0.001486
14.8	0.001728
18	0.001879
21.48	0.002151
25	0.002208
27.5	0.002328
30°	0.002445

The experimental values are very closely reproduced by the equation $\lambda_t = 0.002208 + \beta(t-25) + \gamma(t-25)^2$, where $\beta = 0.0000456$ and $\gamma = 0.0000001626$.

The molecular conductivity of calcium sulphate has been determined, both at 18° and 25°, and it is found that at the former temperature μ_∞ has a value about 240. The relation between the specific conductivity of a calcium sulphate solution at 25° and its concentration c (in milligram mols. per litre) is given by the equation $c = -0.354 + 5211 \lambda + 841400 \lambda^2$.

The author has used Arrhenius' form of resistance cell, and emphasises the need for setting the electrodes always in the same position relatively to one another and to the containing vessel. From this point of view, he considers it an advantage to have the lower part of the resistance cell of a conical shape, so that the lower electrode may rest on its walls.

J. C. P.

Suggested Theory of the Aluminium Anode. W. W. TAYLOR and J. K. H. INGLIS (*Phil. Mag.*, 1903, [vi], 5, 301—313).—Aluminium is rapidly attacked by dilute hydrochloric acid, very slowly by dilute sulphuric acid; addition, however, of a soluble chloride to the sulphuric acid produces violent action. It is further known that when

aluminium acts as anode in a cell containing sulphuric acid or a sulphate as electrolyte, there is a very great resistance to the passage of the current, owing to the formation of an aluminium hydroxide film on the anode. The authors have studied the way in which the current in such a cell as that just described is affected by the addition of chloride, bromide, nitrate, acetate, chlorate, and thiocyanate, and, finding that addition of any of these (acetate excepted) led to the ready passage of a current, they suggest that a film of aluminium hydroxide is impermeable to SO_4^{--} and Al^{+++} ions. This would accord with the fact that when the aluminium is made the cathode in the cell above referred to, the current passes readily. By means of an aluminium hydroxide film deposited in a gelatin membrane, the rates of diffusion of potassium chloride, bromide, nitrate, chlorate, thiocyanate, and sulphate have been compared; with the exception of the sulphate, all passed rapidly through the film. It was found possible to reproduce the peculiarities of a cell with an aluminium anode by taking two platinum electrodes separated by an aluminium hydroxide film, the latter being deposited in the wall of a porous pot.

Experiments were made to see whether the salts which affect the behaviour of an aluminium electrode are also those which accelerate the solvent action of sulphuric acid on aluminium. Addition of potassium chloride very markedly increased the volume of gas liberated in a given time, but potassium bromide had very little influence on the rate of action. J. C. P.

Variation of Electrolytic Conductivity with Temperature below 0° . JAKOB KUNZ (*Zeit. physikal. Chem.*, 1903, 42, 591—596).—As Kohlrausch has shown in a recent paper (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 42, 1026; see also Bousfield and Lowry, this vol., ii, 52), the curves expressing the relation between temperature and electrolytic conductivity will, if produced, cut the temperature axis at about -39° . The author has determined the conductivity of (1) eleven solutions of sulphuric acid (containing from 19—70 per cent. H_2SO_4), (2) two solutions of calcium chloride (25.5 and 29 per cent.), (3) two solutions of sodium hydroxide (27.1 and 32.7 per cent.) at temperatures far below 0° , in some cases even as low as -70° . Instead of converging on one point, the conductivity-temperature curves approach the temperature axis more and more slowly as the temperature falls; and they would cut it probably only at the absolute zero if crystallisation did not take place previously. The empirical expression, $K_t = K_0(1 + \alpha t + \beta t^2)$, which has been useful in giving the relation of conductivity and temperature above 0° , does not represent the course of the curves at low temperatures; below -35° , the conductivity diminishes more slowly than the above formula demands. J. C. P.

Formation of Metallic Oxides. II. Anodic Oxidation of Metals and Electrolytic Development of Oxygen. ALFRED COEHN and YUKICHI OSAKA (*Zeit. anorg. Chem.*, 1903, 34, 86—102. Compare this vol., ii, 80).—The behaviour of the anode in aqueous solutions in which the anion gives oxygen on discharge may be divided into three groups: (a) it remains unchanged, (b) it dissolves quanti-

tatively according to Faraday's law, (c) it forms an oxide. Metals representing the first and the last group have been examined. The anodic decomposition curves of various metals were determined in a normal solution of potassium hydroxide. A platinum plate was used as cathode, and as anode a metal wire. The potential of the anode was measured against a constant hydrogen electrode and the following results were obtained :

Metal.	Oxidation potential.	Oxygen evolved at metal or at oxide.	Metal.	Oxidation potential.	Oxygen evolved at metal or at oxide.
Au	—	1.75	Cu	0.46	1.48
Pt	—	1.67	Fe	—	1.47
(polished)			Pt	—	1.47
Pd	—	1.65	(platinised)		
Cd	0.48	1.65	Co	0.85	1.36
Ag	1.18	1.63	Ni	—	1.35
Pb	1.4	1.53	(polished)		
			Ni	—	1.28
			(spongy)		

In the table, the metals are arranged according to the potential at which oxygen is evolved from them. The series can be well illustrated by soldering strips of the metals to a copper wire and immersing the system in potassium hydroxide solution ; when a current of increasing *E.M.F.* is passed through, the evolution of oxygen from the metals can be seen. Since platinum shows a particularly high value for the supertension of oxygen, whilst it does not do so for hydrogen, it follows that the power of metals to hinder the free evolution of gases depends not only on the nature of the metal but also on that of the gas.

Glaser (Abstr., 1899, ii, 78) has proved that in the electrolytic decomposition of water at a platinum electrode, the decomposition curve for oxygen shows two changes of direction—at 1.08 volts and at 1.67 volts. The first point is independent of the nature of the metal of the anode. An examination of the curve with anodes of platinum, gold, and nickel shows that change of direction occurs at about 1.14 volts in confirmation of this point. The second point is irreversible and depends on the material of the anode, values varying between 1.28 volts and 1.67 volts having been obtained with the metals examined. When the current is passed through at a lower potential than that required for visible evolution of oxygen, an oxidised substance is obtained in the solution, which is not hydrogen peroxide, and various considerations lead to the view that it is ozonic acid. If the potential be greater than 1.67 volts, the hydroxyl ions are discharged and ozone is formed ; this also is a reversible process like that which takes place at 1.1 volts. In potassium hydroxide solution, no ozone is evolved from a nickel anode, even if the potential be as high as three volts. The electrolytic decomposition of water in potassium hydroxide

solution takes place more easily with nickel electrodes than with platinum. It has also been proved that when nickel is used an oxygen electrode is more quickly obtained, but at the same time the oxygen potential is more quickly lost. By making use of the various super-tensions of oxygen at various metals, organic oxidations may be carried out step by step. J. McC.

Determinations of Constitution by Qualitative Migration Experiments. GEORG BREDIG (*Zeit. anorg. Chem.*, 1903, 34, 202—204).—A reply to Kremann (this vol., ii, 54). It has already been shown by Winkelblech (*Abstr.*, 1901, ii, 370) that methyl-orange cannot produce any appreciable quantity of cathions in acid solution.

Kremann's results may be interpreted according to the author's definition of an "inner salt" (*Abstr.*, 1894, ii, 229) by assuming that the basic function of methyl-orange only comes into action by the addition of hydrogen ions to the yellow sulphonic acid ion, $\text{Me}_2\text{NRSO}_3'$, when the electrically neutral, non-migratory ion, $\text{HMe}_2\text{NRSO}_3'$, is formed. Winkelblech has also shown that in a series of amphoteric electrolytes the stronger acid is sometimes also the stronger base, but Kremann is mistaken in believing that this is always the case.

Kremann's qualitative result in showing that in alkaline solution zinc and chromium migrate to the anode, does not necessarily prove that zinc or chromium anionic complexes are present, because, as Picton and Lindner (*Trans.*, 1892, 61, 160) and others have shown, such migration takes place in colloidal solutions, and the direction of the migration depends on the medium (Hardy, *Abstr.*, 1900, ii, 396).

These qualitative migration experiments can only be applied to the solution of constitution problems in conjunction with other physico-chemical methods. J. McC.

The Decomposition Curves of Solutions of Copper Salts. M. E. HEIBERG (*Zeit. Elektrochem.*, 1903, 9, 137—139).—The cathodic decomposition curve of solutions of copper sulphate always shows a rise beginning about 0.1 volt before the decomposition point of copper sulphate is reached. Variations in the purity and method of preparation of the salt used or of the sulphuric acid added makes no difference to this phenomenon, but it is better marked in solutions containing much cuprous salt, and may be made to disappear by repeated electrolysis (by means of which cuprous ions are removed). The rise of current is therefore due to the discharge of cuprous ions. Solutions of silver nitrate do not behave in this way. T. E.

Ionisations of Gases. P. LANGEVIN (*Ann. Chim. Phys.*, 1903, [vii], 28, 289—384. Compare *Abstr.*, 1902, ii, 301).—A detailed historical and critical account of the various researches on the ionisation of gases is given. The author describes fully his own experiments, the results of which have been previously communicated (*loc. cit.*), on the ionisation produced on the one hand by the Röntgen rays and on the other by the cathode rays, and discusses at considerable length their bearing on the work of other investigators in the same field.

K. J. P. O.

Thermomagnetic and related Properties of Crystalline Bismuth. LOUIS LOWNDS (*Phil. Mag.*, 1903, [vi], 5, 141—153).—The resistance of bismuth in directions along and perpendicular to the chief crystallographic axis was determined at temperatures of -79° , -186° , and at the room temperature (22.5° or 14°) in electric fields varying from 2120 to 4980 C.G.S. units. The percentage augmentation of resistance increases more rapidly than the strength of the field and is greater in the direction parallel to the crystallographic axis. It increases as the temperature falls, but reaches a maximum, and for strong fields the variation of resistance is greater at -79° than at -186° , the greatest increase obtained being 62.1 per cent. The Hall effect was also investigated at the same temperatures. The magnetic field was always at right angles to the plate of bismuth and hence to the crystallographic axis, and the current either along or at right angles to the axis, the *E.M.F.* in a direction perpendicular to the current was measured by a compensation method. The effects differed little for the two directions of the current, and at the ordinary temperature there is little dissymmetry for opposite directions of the field; at low temperatures, however, the dissymmetry is more marked. The thermal conductivities perpendicular and parallel to the crystallographic axis were found to be in the ratio 1.42 in zero field and 1.80 in a field of 4980 C.G.S. units, the corresponding values for electrical conductivity being 1.78 and 1.87. L. M. J.

Zero of the Centigrade Thermometer on the Absolute Scale. J. A. GROSHANS (*Zeit. physikal. Chem.*, 1903, 42, 626—628).—According to the author, $T = K\sqrt{x} \cdot A/B$, where T is the boiling point (absolute) of a substance with molecular weight A , and "density number" B (compare Abstr., 1901, ii, 644); K is a constant and x is a simple number varying regularly in a homologous series. A similar expression is given for the melting point, and by comparing the boiling points and melting points of various compounds, the author claims to be able to calculate the point on the absolute scale corresponding with 0° C. J. C. P.

Temperature of Calefaction and its Employment in Alcoholometry. BORDIER (*Compt. rend.*, 1903, 136, 459—461).—When a metal plate, over which a drop of a liquid is in the spheroidal state, is cooled, a point is arrived at at which the liquid comes into contact with the metal and is vaporised. This is termed the *point of calefaction*, and is a physical constant dependent on the nature of the liquid. The determination of this point is made by allowing the liquid to drop from a Mohr burette from a height of 25 mm. on to a heated nickled copper plate. The plate possesses a cavity which is filled with mercury, and the temperature is observed on an immersed thermometer. The determination of the point at which the spheroidal state ceases can be conveniently used as a means of ascertaining the strength of aqueous alcohol. The calefaction point of water is 178° , and that of alcohol 128° . It is worthy of note that the temperature difference is 50° , whilst the boiling points lie only 22° apart. The following cale-

fraction points have been determined for mixtures of alcohol and water :

Percentage of alcohol.	Point of calefaction.	Percentage of alcohol.	Point of calefaction
0	178°	28·6	154·5°
1	177	37·6	150·5
3	175·5	48·6	144·5
5	173·5	58·6	141·0
9·15	169·5	70	137
15·3	164	80	134
19·8	161·25	90	131·2
24·5	157·2	100	128

When these results are represented graphically, a smooth curve is obtained. The advantage of the method is that it can be carried out quickly, and only 1—2 c.c. of liquid is required. J. McC.

Specific Heats of Metals and the Relation of Specific Heat to Atomic Weight. II. WILLIAM A. TILDEN (*Proc. Roy. Soc.*, 1903, 71, 220—221. Compare Abstr., 1900, ii, 524).—The mean specific heats of pure aluminium, nickel, cobalt, silver, and platinum have been determined for several ranges of temperature, with the results shown below :

Range.	Aluminium.	Nickel.	Cobalt.	Silver.	Platinum.
-182° to +15°	0·1677	0·0838	0·0822	0·0519	0·0292
-78 „ +15	0·1984	0·0975	0·0939	0·0550	—
+15 „ 100	—	0·1084	0·1030	0·0558	0·0315
15 „ 185	0·2189	0·1101	0·1047	0·0561	—
15 „ 335	0·2247	—	—	—	—
15 „ 350	—	0·1186	0·1087	0·0576	—
15 „ 435	0·2356	0·1240	0·1147	0·0581	0·0338
15 „ 550	—	0·1240	0·1209	—	—
15 „ 630	—	0·1246	0·1234	—	—

From these values, the specific heats at successive temperatures on the absolute scale have been calculated. The results thus obtained are in conflict with the assumption of a constant atomic heat at absolute zero.

The mean specific heat of a sample of nickel steel containing 36 per cent. of nickel and having a very small coefficient of expansion varied with the range of temperature employed similarly to pure nickel.

The mean specific heats of nickel sulphide and silver sulphide were determined with the following results

Range.	Nickel sulphide	Silver sulphide
-182° to +15°	0·0972	0·0568
15 „ 100	0·1248	0·0737
15 „ 324	0·1333	0·0903

J. C. P.

Liquid Baths for Melting Point Determinations. HEYWARD SCUDDER (*J. Amer. Chem. Soc.*, 1903, 25, 161—163).—A mixture prepared by boiling seven parts by weight of sulphuric acid of sp. gr. 1.84 with three parts of potassium sulphate for five minutes has been found suitable. It can be heated to 325° without boiling. For temperatures from 360° to 600°, fused zinc chloride has been found to give satisfactory results.
A. McK.

The Course of the Melting Point Lines of Solid Alloys or Amalgams. I. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 424—430).—As the temperatures of fusion of tin and mercury are so different, the melting points of amalgams of those metals extend over a large range of temperature. The author finds that the experimental results of van Heteren (this vol., ii, 216) may be predicted theoretically.
A. McK.

Application of the Phase Rule to the Melting Points of Copper, Silver, and Gold. THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1903, 42, 617—620).—The greater part of this paper has been previously abstracted (*Abstr.*, 1902, ii, 455).

In connection with the lower melting point of copper at 1065°, experiments have shown that copper saturated with cuprous oxide contains 2.16 per cent. of the latter. On the assumption that the copper molecule is monatomic and that the solute is not polymerised, the latent heat of fusion of copper is calculated to be 30 cal., a value much smaller than that (43 cal.) found by J. W. Richards.

The terms 'invariant,' 'univariant,' and 'bivariant,' are recommended in preference to the older ones, 'non-variant,' 'monovariant,' and 'divariant.'
J. C. P.

Apparatus for Continuous Vacuum Distillation. CHARLES F. MABERY (*Amer. Chem. J.*, 1903, 29, 171—173).—An apparatus is described which provides for the exclusion of air from the hot oil in the still during the change of receiver, for the admission of distillates into the still without interruption, for the admission of air into the receiver before removal of each fraction, and for the exhaustion of the receiver for the new fraction without connection with the still. For details, the description and diagram in the original must be consulted.
E. G.

The Prevention of Bumping. HEYWARD SCUDDER (*J. Amer. Chem. Soc.*, 1903, 25, 163—165).—A single glass capillary tube has been found to be effective, and introduces into the liquid no foreign substance except glass and one small air-bubble. The open end should rest on the bottom of the flask; the tube should be sealed about 1 cm. above this and again at the top, and its length should be such that the upper end reaches nearly to the top of the neck of the flask.
A. McK.

Simple Relation between the Molecular Heat of Solidification and the Boiling Point. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1903, [vii], 28, 384—422. Compare Abstr., 1901, ii, 372, 594, 641; and 1902, ii, 379).—In this paper, the author has collected and arranged in their logical sequence the results of a series of researches which have been previously published bearing on the relation between the molecular heat of solidification and the boiling point, expressed by the equation, $(L + S)/T = Q/T' = K$, where L is the latent heat of evaporation, S the latent heat of solidification, and Q the latent heat of sublimation; T and T' are respectively the absolute temperatures at which the vapour pressures in sublimation and vapourisation are equal to the atmospheric pressure.

The paper contains an historical and critical account of the previous work on the same subject by other investigators. K. J. P. O.

Relation between Freezing Points, Boiling Points, and Solubility. MEYER WILDERMANN (*Zeit. physikal. Chem.*, 1903, 42, 481—496).—If C is the concentration of the saturated solution and ρ the heat of solution, then $d(\log_e C)/dT = \rho/2T^2$, as shown by le Chatelier and van't Hoff. The former of these two investigators has pointed out that the solubility curve given by this equation must have a maximum, that is, above a certain point the solubility diminishes with rising temperature. Now on the curve connecting the freezing point of a solution with the concentration (that is, the freezing point curve), the concentration increases with falling temperature; on the curve connecting the boiling point of a solution with temperature (that is, the boiling point curve), the concentration increases with rising temperature. Hence, provided the solute is non-volatile, the solubility curve will be cut both by the freezing point and boiling point curves. At the point of section (T_1) of the solubility and freezing point curves, there will be present solid solute, solid solvent, and saturated solution; at the point of section (T_1') of the solubility and boiling point curves, there will be present solid solute, saturated solution, and vapour of the solvent. On the basis of these relations, the author shows that for aqueous solutions the solubility curve can be calculated from T_1 , ρ_1 , M , the molecular weight of the solute, and T_0 , the freezing point of the pure solvent, by the equation:

$$\log C = -\frac{\rho}{4 \cdot 6052} \left(\frac{1}{T} - \frac{1}{T_1} \right) + \log(T_0 - T_1) + \log \frac{M}{18 \cdot 7}.$$

If the solute is an electrolyte, the factor i must also be known.

A similar equation holds for the relation of solubility and boiling point curves. The equations have been tested in the case of aqueous solutions of boric acid and potassium chlorate, and a good agreement was found between the calculated and experimentally determined values of the solubility.

Further, if T_0' be the boiling point of the solvent, λ and l its latent heats of fusion and vaporisation respectively, the following relation exists between the various constants:

$$\frac{\rho}{4 \cdot 6052} \left(\frac{1}{T_1} - \frac{1}{T_1'} \right) = \log \frac{T_1' - T_0'}{T_0' - T_1} + \log \frac{l \cdot T_0'}{\lambda \cdot T_0'^2}.$$

For boric acid, the left hand side of this equation has the value 1.18, the right hand side has the value 1.15—1.16. The heat of solution p has been regarded throughout as independent of the temperature.

J. C. P.

Relation between Constitution and Cryoscopic Behaviour of Solvents. KARL AUWERS [with G. MANN and E. GIERIG] (*Zeit. physikal. Chem.*, 1903, 42, 513—544. Compare Abstr., 1900, ii, 66).—The following p -derivatives of toluene have been used as solvents: p -xylene (depression constant, $K=43$), p -chlorotoluene ($K=56$), p -bromotoluene ($K=82$), p -iodotoluene ($K=113$), p -nitrotoluene ($K=78$), p -toluidine ($K=53$), methyl p -toluate ($K=62$). Toluene, the parent substance, cannot be employed for cryoscopic investigations, but the influence of the methyl group is very slight, and, accordingly, benzene is taken as the standard of abnormalising power. As solutes, the following have been used: methyl o -hydroxybenzoate, o -, m -, and p -cyanophenols, formanilide, o - and p -formotoluidides, formo- p -anisidide. When the molecular weights of these solutes are determined in the above-mentioned solvents, it is found that the tendency to give abnormally high molecular weights is hardly affected by the introduction of a halogen atom or methyl group into the ring; this tendency is, however, markedly diminished by the introduction of the groups --NO_2 , $\text{--CO}_2\text{Me}$, and --NH_2 ; indeed, the molecular weights obtained with p -toluidine as solvent are nearly normal.

Further experiments with dichloro- and dibromo-benzenes as solvents show that the introduction of a second halogen atom effects a noticeable reduction in the abnormalising power of benzene.

Another point dealt with is the comparative behaviour of benzene and naphthalene in relation to phenols, alcohols, acids, amides, amines, and nitroso-compounds as solutes. The numerous experimental data obtained show that the abnormalising power of benzene is considerably greater than that of naphthalene.

If the ordinary substituent atoms or groups are arranged as follows, CH_3 , Cl , Br , I , NO_2 , CO_2R , CN , CHO , NH_2 , CO_2H , OH , it is to be noted that, when introduced into a solvent, each diminishes the tendency to cryoscopic abnormality more than the one immediately preceding; when substitution takes place in the solute, the opposite is the case.

J. C. P.

Cryoscopic Notes. KARL AUWERS [with E. GIERIG] (*Zeit. physikal. Chem.*, 1903, 42, 629—631).—The effect of α - and β -naphthols, p -nitro- α -naphthol, β -nitro- α -naphthol, and α -nitro- β -naphthol on the freezing point of p -dibromobenzene has been determined. The latter is recommended as a solvent for the investigation of abnormal cryoscopic behaviour; it readily dissolves most substances and has a high depression constant ($K=124$). There seems to be no marked difference between α - and β -naphthols, the molecular weights found for the two substances in equally concentrated solutions being nearly the same. A nitro-group in the o -position does not appear to exert any special influence, but with a nitro-group in the p -position there is a marked

departure from the normal behaviour, as has been found to be the case also with monocyclic phenols.

Fresh attempts to obtain consistent results with *p*-azoxyanisole as solvent have failed; its depression constant was found in most cases to lie between 500 and 700 (compare Auwers, *Abstr.*, 1900, ii, 262).

J. C. P.

Clarke's New Thermochemical Constant. WOLF VON LOEBEN (*Zeit. anorg. Chem.*, 1903, 34, 174—179).—The author discusses the equation $4K/(12a + 6b - c - 8n) = \text{constant}$, deduced by Clarke (this vol., ii, 8). It is shown that in this deduction Clarke has argued in a circle, and the constant cannot, therefore, be regarded as a truly natural one. Furthermore, as isomerides have in many cases appreciably different heats of combustion, and as this is not allowed for in the formula, constant values are not obtained.

J. McC.

Calculation of Thermochemical Results. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1903, 25, 209—214).—During a chemical reaction, the heat capacities of the reacting substances change, but the magnitude of such changes and their significance are often neglected. Greater accuracy in the calculation of thermochemical data ought to be aimed at. All thermochemical data ought to be reduced to their isothermal values at some definite temperature, so that they may be strictly comparable.

A. McK.

Heats of Formation of some Compounds containing Sulphur and Nitrogen. MARCEL DELÉPINE (*Compt. rend.*, 1903, 136, 451—453).—The heats of combustion of the following compounds were determined with the Berthelot calorimetric bomb, and from the results the heats of formation from the elements have been calculated.

	Heat of combustion (at constant volume).		Molecular heat of formation.
NMe:C(SMe) ₂	966·5	Cal.	+ 0·7 Cal.
NEt:C(SMe) ₂	1126·98	„	+ 3·15 „
NMe:C(SEt) ₂	1285·97	„	+ 7·15 „
NPh:C(SMe) ₂	1541·5	„	− 34·1 „
NMe ₂ ·CS·SMe	951·15	„	+ 16·0 „
NMe ₂ ·CS·SEt	1119·05	„	+ 11·2 „
NEt ₂ ·CS·SMe	1268·3	„	+ 24·8 „
CH ₂ < $\begin{smallmatrix} \text{S} \cdot \text{CH}_2 \\ \text{S} \cdot \text{CH}_3 \end{smallmatrix}$ >NMe	961·73	„	+ 5·45 „
C ₂ H ₄ < $\begin{smallmatrix} \text{S} \cdot \text{C}_2\text{H}_4 \\ \text{S} \cdot \text{C}_2\text{H}_4 \end{smallmatrix}$ >NH	1260·28	„	+ 32·9 „
CS ₂ (CH ₂ :NMe) ₂	1095·77	„	+ 0·3 „
CS ₂ (CHMe:NH) ₂	1083·2	„	+ 12·9 „
CH ₂ < $\begin{smallmatrix} \text{S} \cdot \text{CH}_2 \\ \text{S} \cdot \text{CH}_2 \end{smallmatrix}$ >N·CH ₂ ·N:CH ₂ ..	1110·15	„	− 14·2 „

The heats of formation of the iminodithiocarbonic esters differ by
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about 11 Cal. from the heats of formation of the corresponding thio-carbimides. Other numerical relationships are indicated.

J. McC.

Heat of Combustion of Phosphorus. Phosphoric Oxide. H. GIRAN (*Compt. rend.*, 1903, 136, 550—552).—When phosphorus is burnt in oxygen at a pressure of 10—15 atmospheres, the combustion is complete and nearly instantaneous, phosphoric oxide being formed. The heat of combustion is given by the equation: $2P + 5O = P_2O_5$ (solid) + 369.4 Cal. Andrew's determination (*Phil. Mag.*, 1848, [iii], 32, 321) gave the heat of combustion as +356.31 Cal., and Abria's (*Compt. rend.*, 1846, 22, 372) as +351.48 Cal. In both cases, the combustion was carried out under the ordinary pressure, and doubtless some of the phosphorus escaped combustion. The heat of solution of the phosphoric oxide obtained in these experiments is given by the equation: P_2O_5 (solid) + water = P_2O_5 (dissolved) + 34.37 Cal.; a comparison of this value with Hautefeuille and Perrey's determinations (*Abstr.*, 1884, 1258) of the heat of dissolution of crystalline, amorphous, and vitreous phosphoric oxide shows that the phosphoric oxide formed in the combustion of phosphorus is the amorphous variety.

Measurements of the heat of neutralisation by aqueous sodium hydroxide of the acid produced by dissolving the three forms of phosphoric oxide in cold water demonstrate that metaphosphoric acid alone is formed. From this fact, it follows that the following thermal equations express the change of the different forms of phosphoric oxide into each other: P_2O_5 (crystalline) = P_2O_5 (amorphous) + 6.98 Cal.; P_2O_5 (amorphous) = P_2O_5 (vitreous) + 4.72 Cal. The heat of formation of phosphoric acid from its elements, deduced from the results here recorded and those previously given (this vol., ii, 139) for the heat of transformation of metaphosphoric acid in solution into orthophosphoric acid, is found to be +305.83 Cal. for crystalline, +303.32 Cal. for fused, and +308.53 Cal. for dissolved phosphoric acid. With these new values for the heat of formation of orthophosphoric acid, the heat of formation of pyrophosphoric acid becomes +535.69 Cal. for the crystalline, +533.4 Cal. for the fused, and +543.62 Cal. for the dissolved acid, and the heat of formation of metaphosphoric acid becomes +226.61 Cal. for the solid and +236.37 Cal. for the dissolved acid (compare *loc. cit.*).

K. J. P. O.

Cinchona Alkaloids. Cinchonine, Cinchonidine, and Cinchonamine. MARCELLIN P. E. BERTHELOT and GAUDECHON (*Compt. rend.*, 1903, 136, 181—186. Compare this vol., ii, 197).—The mol. heat of combustion of cinchonine is 2543.3 Cal. at constant volume and 2546.2 Cal. under constant pressure. The heat of formation from its elements therefore amounts to +4.7 Cal. Both the freshly precipitated base and the crystalline variety appear to be in the same molecular condition. The measurement of the heat of neutralisation by various acids has given the following results: the base (1 mol.) + 2HCl (in solution) develops +13.15 Cal., and +HCl, +7.15 Cal.; the base

+ H_2SO_4 develops +15.9 Cal., and + $\frac{1}{2}\text{H}_2\text{SO}_4$, +11.35 Cal.; in the formation of the solid salt, the base (1 mol.) + HCl gas develops +26.1 Cal. The formation of the solid hydrated sulphate (with $2\text{H}_2\text{O}$) develops +19.4 Cal., whence the anhydrous salt has a heat of formation +36.4 - α Cal. Cinchonine is, therefore, a weaker base than quinine.

The heat of combustion of cinchonidine is 2543.6 Cal. at constant volume and 2545.9 Cal. under constant pressure. The heat of formation from its elements is +4.95 Cal. The base + 4HCl (in solution) develops +13.8 Cal., and +HCl about +9 Cal.; + $2\text{H}_2\text{SO}_4$ (in solution) about +16 Cal.; the heat of formation of the solid hydrochloride from gaseous hydrogen chloride is about +26 Cal. The thermochemistry of cinchonidine is identical with that of cinchonine.

The mol. heat of combustion of cinchonamine is 2593.9 Cal. at constant volume and 2596.5 Cal. under constant pressure, and the heat of formation from its elements is +23.4 Cal. Owing to the small solubility of its salts, the heat of neutralisation of the base could not be directly determined. The heat of combustion of the hydrochloride is 2580.5 Cal. at constant volume and 2583.1 Cal. at constant pressure; the heat of formation from its elements is +76.2 Cal.; hence the heat of neutralisation by gaseous hydrogen chloride is +30.8 Cal. The heat of combustion of the nitrate is 2558.6 Cal. at constant volume and 2560.2 Cal. under constant pressure; the heat of formation from its elements is +94.2 Cal., whence the heat of neutralisation by nitric acid (gaseous) amounts to +36.6 Cal. and by nitric acid (solid) to +28.6 Cal. These values are comparable with those given by quinine and ammonia.

K. J. P. O.

Thermal Study of some Alloys of Copper and Aluminium.

II. WLADIMIR F. LUGININ and A. SCHÜKAREFF (*Arch. Sci. phys. nat.*, 1903, [iv], 15, 49—77. Compare Abstr., 1902, ii, 259).—The heat of solution of the alloy has been determined in a solution of bromine in aqueous potassium bromide similar to that employed by Herschkowitsch (Abstr., 1898, ii, 582). It has not been possible to determine the heat of solution of alloys containing more than 50 per cent. of aluminium because with these hydrogen is evolved. The heat of formation of dissolved cupric bromide, calculated from the heat of solution in this liquid, is 39,484 cal., whilst that of aluminium bromide is 202,193 cal. The following heats of formation were found from the difference of the heat of solutions of the alloy and of the single metals: Cu_3Al , 123.5 cal.; Cu_2Al , 137.9 cal.; Cu_3Al_2 , 71.0 cal.; CuAl , 20.8 cal.; Cu_2Al_3 , 48.9 cal.; and CuAl_2 , -57.2 cal. From these results, it would appear that the alloy corresponding with the formula Cu_2Al is formed with the greatest development of heat, and the authors regard this as a definite chemical compound. The alloys were prepared by adding the requisite quantity of aluminium to fused copper; they are brittle and can be reduced to powder.

When aluminium is fused and copper added in the proportion indicated by the formula CuAl_3 and the fused mass is poured on to dry sand, long, needle-shaped crystals separate on cooling. These have been obtained up to 2 cm. long; they have a silvery lustre and a

sp. gr. of 4.042 at 20°. This alloy may be a definite compound and is not identical with the compound, Cu_4Al_9 , described by Brunck (Abstr., 1901, ii, 656). The alloy, CuAl_3 , has a specific heat of 0.1586 (between 20° and 100°), whilst that of Cu_4Al_9 is 0.1502. J. McC.

Variations of the Modulus of Elasticity of Nickel Steels. CH. ÉD. GUILLAUME (*Compt. rend.*, 1903, 136, 498—500).—The thermal variation of the modulus of elasticity of spirals of nickel steel of various compositions has been determined. A steel containing 22 per cent. of nickel and 3 per cent. of chromium is non-magnetic in liquid air; one containing 26.2 per cent. of nickel becomes magnetic at -17°, and one with 27.9 per cent. of nickel at +40°. The maxima of the moduli of these last two steels are at -27° and +30° respectively, that is, at a temperature about 10° below that at which the steel passes from the non-magnetic to the magnetic condition.

J. McC.

Expansion of Fused Quartz. LUDWIG HOLBORN and F. HENNING (*Ann. Physik*, 1903, [iv], 10, 446—448. Compare Holborn and Day, *Ann. Physik*, 1901, 4, 104; Holborn and Grüneisen, *ibid.*, 6, 136).—A rod of fused quartz, 52 cm. long and 2.9 mm. thick, was exposed to temperatures up to 1000° and the change in length determined. It is found that the mean increase of unit length for a rise of 1° is 0.00000054 (compare Le Chatelier, Abstr., 1900, ii, 539; Callendar, *Chem. News*, 1901, 83, 151). The expansion is regular between 0° and 1000°.

J. C. P.

The Phenomena of Adhesion and of Solution [in connection with the precipitation of] Magnesium and Manganous Hydroxides and Barium Sulphate. HARRISON EASTMAN PATTEN (*J. Amer. Chem. Soc.*, 1903, 25, 186—198).—When potassium hydroxide solution is added to a solution of magnesium chloride or of a mixture of the latter with potassium sulphate, the magnesium hydroxide precipitated does not carry down with it either chlorine or sulphur trioxide. Barium sulphate does not carry down either magnesium oxide or chloride. Manganous hydroxide carries down with it sulphur trioxide when it is precipitated from a solution of manganese chloride and potassium sulphate. The bearing of the author's observations on the subject of colloidal solution is discussed.

A. McK.

New Osmotic Membranes prepared by the Electrolytic Process. HARMON N. MORSE (*Amer. Chem. J.*, 1903, 29, 173—174. Compare Abstr., 1901, ii, 543).—The investigation of a large number of electrolytically deposited substances has shown that the following exhibit considerable osmotic activity; the ferrocyanides of zinc, cadmium, manganese, and uranyl, the phosphates of copper and uranyl, and ferric and aluminium hydroxides.

E. G.

Osmotic Pressure of a Solution of Variable Density. MAX PLANCK (*Zeit. physikal. Chem.*, 1903, 42, 584—590).—Supplementary to a previous paper (Abstr., 1902, ii, 597). The author discusses

two definitions of osmotic pressure and their relation to each other. Expressions are deduced thermodynamically connecting the osmotic pressure and the vapour pressure of a solution. J. C. P.

Movements of the Flame in the Explosion of Gases. HAROLD B. DIXON [and, in part, J. BOWER, L. BRADSHAW, B. DAWSON, EDWARD GRAHAM, R. H. JONES, and E. H. STRANGE] (*Phil. Trans.*, A, 1903, 200, 315—352).—After an historical introduction, the author discusses a large mass of photographic evidence bearing on the above subject. By rapid vertical movement of a sensitive film in front of an explosion tube placed horizontally, it has been possible to obtain a photographic record of the propagation of an explosion, and the paper contains about 70 such records obtained under varying conditions of explosion. To appreciate the author's argument fully, reference must be made to the original, with its photographic reproductions.

On the developed film, the detonation wave appears as a sloping line of light; if the end of the tube has been closed, there is depicted also a reflected wave, visible even when the tube has been fractured by the explosion. The photographs demonstrate the sharpness with which the luminosity is set up, and the uniformity of the detonation wave; they show also that the ignited gas remains luminous for some time after the wave has passed. The ratio $\frac{\text{velocity of detonation wave}}{\text{velocity of reflexion wave}}$,

deduced from the slope of the lines on the film, varies for different explosive mixtures from 1.56—2.22. It has been found possible to measure the rate of propagation of a true sound wave in the gases produced by the detonation wave, and there is very close agreement between the velocity of these sound waves and that of the reflexion waves just referred to. This being so, the temperature of the gas where the reflexion wave was measured could be calculated from the known relation between velocity of sound and temperature. Thus the velocity of the reflexion wave in an exploded mixture of cyanogen and oxygen (equal volumes) was found to be 1230 metres per second. Assuming that γ , the ratio of the specific heats, is independent of temperature, it follows that the gas where the reflexion wave was measured was at a temperature of 3330°. If, however, the value of γ has fallen to 1.29 (Le Chatelier), the temperature of the gas was 3672°.

Interesting photographs were obtained showing that when one detonation wave meets another it gives rise to a reflected wave rather less rapid than itself and not so luminous; further, this reflected wave appears to have a greater velocity than that obtained at a metal surface.

Many of the photographs show that the detonation wave starts with an abrupt spring, and that from its starting point a strongly luminous wave is thrown back through the ignited gases. This "retonation wave," as the author terms it, is often closely similar to the detonation wave; it attains its greatest rapidity and brightness when it is produced at the end of a tube, so that the reflexion wave is superposed.

As regards the initial phases of an explosion, some of the photographs show that the initial flame has been overtaken by a bright and

faster flame, others that the advance of the initial flame has been checked. This is attributed to the compression wave set up by the spark; at the beginning of the explosion, the compression wave moves in front of the flame, and if the firing point is near the end of the tube the compression wave is reflected before being overtaken, and in its return checks the advancing flame. If, on the other hand, the firing point is in the middle of the tube, the flame will overtake the compression wave before the latter is reflected. Much photographic evidence is brought forward in support of this explanation.

The author argues against Le Chatelier's view that there is an invisible wave moving in front of the visible wave and with an equal velocity.

J. C. P.

Lecture Experiments to Demonstrate the Law of Mass Action. A. VON DIETERICH and LOTHAR WÖHLER (*Zeit. anorg. Chem.*, 1903, 34, 194—197).—If a $N/1000$ solution of potassium hydroxide, to which phenolphthalein has been added, be shaken with mercurous chloride, the red colour disappears on account of neutralisation and the mixture becomes grey on account of the formation of mercurous hydroxide ($\text{HgCl} + \text{OH}' = \text{HgOH} + \text{Cl}'$). With a $N/100$ solution of potassium hydroxide, mercurous chloride becomes grey, but the red colour produced by phenolphthalein is not destroyed because the chlorine ions reach such a concentration that the above reaction is reversed. The addition of potassium chloride produces the same effect on the $N/1000$ solution of potassium hydroxide. If a few drops of a saturated solution of potassium chloride be added to the dilute potassium hydroxide solution which has been shaken with mercurous chloride, the red colour is reproduced. A mixture of equal volumes of $N/100$ potassium hydroxide solution and saturated potassium chloride solution has no action on mercurous chloride, which remains perfectly white.

If any of these solutions, to which mercurous chloride has been added without causing the disappearance of the red colour of the phenolphthalein, be warmed, the red colour disappears and reappears on cooling.

The similar results obtained by Richter (*Chem. Zeit.*, 1902, 26, 1234) with potassium stearate, elaidate, and oleate can easily be explained by hydrolysis and mass action.

J. McC.

The Equilibrium $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$. OSCAR HAHN (*Zeit. physikal. Chem.*, 1903, 42, 705—708).—Mixtures containing different proportions of the reacting gases were passed through vessels provided with capillary entry and exit channels and containing platinum in a finely divided form or as thin foil. In each experiment, the rate at which the gas was passed was diminished until an alteration in the rate was without effect on the composition of the system. The equilibrium at 1000° has been reached from both sides. For the equilibrium constant, $K = [\text{CO}][\text{H}_2\text{O}]/[\text{CO}_2][\text{H}_2]$, the following values have been obtained:

$t^{\circ} C.$	$K.$	$t^{\circ} C.$	$K.$
786	0.81	1086	1.95
886	1.19	1205	2.10
986	1.54	1405	2.49
1005	1.68		

Using van't Hoff's equation, $d(\log_e K)/dT = -q/RT^2$, and taking $q = -10232 + 0.1685T + 0.00101T^2$, for which latter formula the experimental data of Berthelot and of Mallard and Le Chatelier have been employed, the author finds values for K in good agreement with experiment, the integration constant having been deduced from the value of K at 986° . There are deviations between the calculated and experimental values at the two highest temperatures, possibly owing to dissociation of carbon dioxide and water vapour, or to displacement of the equilibrium during cooling. J. C. P.

Compensation Method of Determining the Rate of Oxidation of Hydrogen Iodide. JAMES M. BELL (*J. Physical Chem.*, 1903, vii, 61—83).—The method adopted by Harcourt and Esson for the determination of the rate of oxidation of hydrogen iodide by hydrogen peroxide (this *Journal*, 1867, 20, 467) consisted in the addition of successive portions of sodium thiosulphate to the solution containing hydrogen peroxide, hydrogen iodide, and a little starch and the observation of the time elapsing after each addition before the blue colour appears. Such a process the author terms a compensation method, and it evidently assumes the absence of other reactions as the direct oxidation of the thiosulphate, or acceleration or retardation of the reaction by its presence. Harcourt and Esson assured themselves of the absence of such reactions, but the method has been subsequently used without any investigations to guarantee its applicability. The author has therefore investigated the reaction with various oxidising agents. With hydrogen peroxide, the method appears to be applicable; with chloric acid, however, this is not the case, the thiosulphate being rapidly oxidised, but the rate of oxidation is greatly retarded by the presence of potassium iodide—an advantage when the thiosulphate is employed in a compensation method. With chromic acid, also, the method is inaccurate, the presence of the thiosulphate affecting the rate of oxidation. L. M. J.

Rate of Reaction in Solutions containing Potassium Iodide, Potassium Chlorate, and Hydrochloric Acid. W. C. BRAY (*J. Physical Chem.*, 1903, 7, 92—117).—Experiments were made in which the concentration of the reactive substances varied within considerable limits, and it is found that the rate at which iodine is liberated in the above solutions is proportional to the concentration of the chlorate and to the square of the concentration of the hydrogen ion (between concentration $C=5$ and $C=20$) and is a linear function of the concentration of the chlorine ion and of that of the potassium iodide. This corresponds with the equations: $\text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+ = \text{ClO}_2\text{H} + \text{ClOH}$, $\text{ClO}_3^- + \text{I}^- + 2\text{H}^+ = \text{ClO}_2\text{H} + \text{IOH}$, followed by instantaneous oxidation

of hydriodic acid by these products. The temperature coefficient corresponds with the doubling of the rate every 8.6 degrees. Ferrous sulphate in small quantities was found to produce a very great acceleration.

L. M. J.

The Velocity of Transformation of Carbon Monoxide. ANDREAS SMITS and LUDWIG K. WOLFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 417—424).—From a study of the catalytic action of iron, nickel, and cobalt respectively on the system $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, Boudouard (*Abstr.*, 1901, ii, 646) has found that at 1000° carbon dioxide in contact with carbon is almost entirely converted into carbon monoxide, whilst at 445° the reverse change takes place almost completely. The authors have examined the conditions of the action below 445°, when carbon monoxide is in a metastable condition. The catalyser used was finely divided nickel. When the nickel was prepared by reduction of the oxide at 310°, its activity varied in successive determinations owing to the gradual deposition of carbon; satisfactory results were, however, obtained when the reduction was conducted at 445°, the metal being already coated with carbon. Observations made at 256°, 310°, and 340° by the aid of the methods of van't Hoff and of Noyes indicated that the action was unimolecular. The reaction constants, calculated from $K = 1/t \log P_0/2P_t - P_0$, were determined at 256°, 310°, and 340°, the values being 0.000279, 0.00186, and 0.00527 respectively. During those measurements, the activity of the catalyser had not diminished. With reference to the mechanism of the action, the two following hypotheses are adduced, firstly, (1) $\text{CO}_2 = \text{CO} + \text{O}$ (with measurable velocity), (2) $\text{CO} + \text{O} = \text{CO}_2$ (with immeasurable velocity); secondly, (1) $\text{CO} + \text{Ni} = \text{C} + \text{NiO}$, (2) $\text{CO} + \text{NiO} = \text{CO}_2 + \text{Ni}$. In the latter case, the second stage takes place more quickly than the first, but it need not be assumed that the velocity of one of the stages is immeasurable.

The catalyser was actually nickel and not the carbon with which it was mixed.

A. McK.

Velocity of Action of Bromine on Ethyl Alcohol. STEFAN BUGARSZKY (*Zeit. physikal. Chem.*, 1903, 42, 545—566).—The course of this reaction has been studied at 0°, 10°, 20°, and 30°, and thus the influence of temperature on the constants k and K (*Abstr.*, 1902, ii, 9) has been determined. The ratio k_{T+10}/k_T for the range of temperature employed has a value about 3, and the variation of k with temperature is found to be adequately represented by the equation $\log_{10} k = 0.04753t - 2.1552$. The variation of K with temperature is satisfactorily given by the linear equation $K = 0.00204 + 0.0000975t$. With the help of van't Hoff's formula, $d(\log_e K)/dT = -q/RT^2$, the author has calculated q , the heat of dissociation of hydrogen tribromide into hydrogen bromide and bromine, and found it = -6026 cal.; actual determination gave $q = -6035$ cal.

J. C. P.

Coupling of Chemical Processes. I. N. SCHILOW (*Zeit. physikal. Chem.*, 1903, 42, 641—689. Compare Thiele, *Abstr.*, 1893, ii, 317; Wagner, *Abstr.*, 1899, ii, 275; Schaer, *Abstr.*, 1902, ii, 603; Manchot, this vol., ii, 151, 152).—Coupled processes are those in

which a slow reaction between two substances, *A* and *B*, is accelerated by a simultaneous rapid action between *A* and *C*, where *C* is a third substance. A particular case of this phenomenon is furnished by the intensifying ('*Activierung*') of oxygen, and this, as well as the fresh cases studied by the author, is to be regarded as an example of 'chemical induction.' Thus bromic acid in dilute aqueous solution oxidises sulphurous acid immediately, but has practically no oxidising action on arsenious acid by itself; if, however, sulphite be added to a mixture of bromic and arsenious acids, a part of the arsenious acid is oxidised also. The reaction between bromic and sulphurous acids is the primary spontaneous reaction; that between bromic and arsenious acids is the secondary induced reaction. The substance taking part in both these reactions (bromic acid in the case mentioned) is termed the 'actor'; the substance taking part only in the primary reaction (sulphurous acid) is the 'inductor'; the substance taking part only in the secondary reaction is the 'acceptor' (compare Manchot, *loc. cit.*). In the investigation of the cases of 'chemical induction' described below, the author has often had occasion to determine the 'induction factor,' by which is to be understood the ratio (quantity of acceptor transformed):(quantity of inductor transformed).

The cases studied by the author are:

(1) Tartaric acid (actor) + chlorine (inductor) + copper oxide (acceptor). Fehling's solution, when treated with small quantities of chlorine (or hypochlorite), deposits cuprous oxide. The induction factor, obtained by comparing the quantity of cuprous oxide formed with the quantity of hypochlorite used, is found to diminish as the concentration of the hypochlorite increases. Hydrogen peroxide and ozone have been found to behave in the same way as chlorine or hypochlorite. The explanation of the phenomenon probably lies in the ability of the hydroxy-acids to give oxidation products which are strong reducing agents.

(2) Ammonia (actor) + hypochlorite or hypobromite (inductor) + permanganate (acceptor). Ammonia and permanganate react slowly, but when the reaction between ammonia and hypochlorite takes place in presence of permanganate, the volume of gas liberated is smaller than it would otherwise be; at the same time, considerable quantities of nitrous acid have been formed, and this is the measure of the action between ammonia and permanganate induced by the primary action between ammonia and hypochlorite. The induction factor diminishes as the concentration of hypochlorite (relatively to permanganate) increases. Silver oxide may take the place of permanganate as acceptor, in which case metallic silver is precipitated (compare Thiele, *loc. cit.*). Further, it has been found that hypochlorite imparts strong reducing properties, not only to ammonia, but also to carbamide, and Luther has observed that anodic reduction of permanganate by ammonia takes place only in presence of Cl^- ions. The active substance which couples the primary and induced reactions in the above case is probably a labile complex formed from the actor and the inductor.

(3) Chromic acid (actor) + arsenious acid (inductor) + tartaric

acid (acceptor). As the concentration of the tartaric acid (relatively to the arsenious acid) increases, the induction factor increases also. Other acids, such as malic, lactic, mandelic, and citric acids, may take the place of tartaric acid as acceptor. It is probable that a stable complex (analogous to tartar emetic) is formed between the arsenious and the oxy-acids.

A variation of the above is obtained by taking sulphurous acid as inductor in place of arsenious acid, but the reaction is irregular. Reference is made to the analogous case in which the oxidation of hydroxy-acids by permanganate is accelerated by the presence of reducing agents such as sulphurous acid, arsenious acid, stannous chloride, and ferrous salts.

(4) Bromic acid (actor) + hydrogen bromide (inductor) + arsenious acid (acceptor). The reaction between potassium bromate and arsenious acid is started by a very small quantity of Br' ions or by a considerable quantity of H' ions; once the reaction has started, it proceeds until all the arsenious acid has been oxidised, showing the phenomenon of initial acceleration; that is, if the quantity of oxidised arsenious acid be plotted against the time, the resulting curve is at first convex to the time axis, and then concave, there being a point of inflexion. This is probably due to the fact that the concentration of Br' ions increases during the reaction, and it is found that the course of the oxidation is in accordance with the equation $dx/dt = K(B+x)(A-x)$, where A and B are the initial concentrations of bromic and hydrobromic acids respectively, and x corresponds with the reduced bromic acid. This formula is based on the following assumptions: (a) that the reaction is of the second order, thus: $\text{HBrO}_3 + \text{HBr} = \text{HBrO} + \text{HBrO}_2$ (compare Judson and Walker, Trans., 1898, 73, 410); (b) that the oxidation of arsenious acid by the system $\text{HBrO} + \text{HBrO}_2$ is instantaneous, and accordingly exerts no influence on the velocity equation; (c) that the reaction between bromic and arsenious acids is extremely slow. These views are supported by the fact that alteration in the concentration of the arsenious acid has practically no effect on the velocity constant; further, the position of the inflexion point can be satisfactorily predicted from the formula. The whole reaction is thus a case of "self-induction," inasmuch as the inductor is formed in the course of the reaction.

(5) Bromic acid (actor) + sulphurous acid (inductor) + arsenious acid (acceptor). In the reaction involving these three substances, two sharply marked stages may be detected; (i) the first 10–15 minutes necessary for the complete oxidation of the sulphurous acid; during this time, the concentration of the arsenious acids rapidly diminishes, although bromic and arsenious acids alone are practically unaffected by each other; (ii) the subsequent period, during which the arsenious acid is oxidised more slowly, in virtue of the reaction (described above) between the bromic acid and the hydrobromic acid produced in the first stage. The oxidation in the first stage is a case of chemical induction, and the induction factor depends chiefly on the relative concentrations of the arsenious and sulphurous acids, increasing with the ratio $C_{\text{As}_2\text{O}_3}/C_{\text{SO}_2}$. Formaldehyde may take the place of sulphurous acid as inductor, but the reaction between

bromic acid and formaldehyde is slow, and the two stages referred to above are not so sharply divided; they are very marked, however, when ferrous oxide acts as inductor. The active substance in this reaction is probably a labile oxidation product of the actor or inductor.

(6) Arsenious acid (actor) + chromic acid (inductor) + bromic acid (acceptor). When the amount of oxidised arsenious acid is plotted against the time, there are two distinct branches of the curve; the first is very steep, corresponding with the period of real induction; the second is nearly a straight line, slightly inclined to the time axis, and representing the oxidation of arsenious acid under the influence of bromic and hydrobromic acids (see above). The induction factor remains practically constant in spite of wide variations in the conditions. J. C. P.

Dissociation of Salts of Heavy Metals. I. Mercury-Nitrogen Salts. HEINRICH LEY and KONRAD SCHAEFER (*Zeit. physikal. Chem.*, 1903, 42, 690—704).—The greater part of this paper has been already abstracted (Abstr., 1902, ii, 357).

The reaction between mercuric chloride and succinimide is reversible, and may be represented by the equation: $\text{HgCl}_2 + \text{HN}:\text{C}_4\text{H}_4\text{O}_2 \rightleftharpoons \text{Cl}\cdot\text{Hg}\cdot\text{N}:\text{C}_4\text{H}_4\text{O}_2 + \text{H} + \text{Cl}'$, and if this is so, then $k = x^3/v(1-x)(n-x)$, where n is the number of molecules of succinimide acting on 1 molecule of sublimate, and x is the extent to which the sublimate has been decomposed. Since the hydrogen chloride is the only constituent of the system that is a conductor, x may be determined from the conductivity. The values thus arrived at for k are satisfactorily constant.

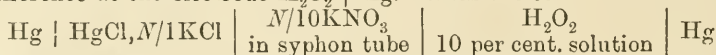
The author's general conclusion that the mercury-imide compounds are more stable than the mercury-amide compounds is in agreement with Kieseritzky's results (Abstr., 1899, ii, 395). J. C. P.

Maxima and Minima of the Decomposition Curves for Hydrated Mixed Crystals. REINHARD HOLLMANN (*Zeit. physikal. Chem.*, 1903, 42, 597—600).—A revised discussion of some points raised in a previous paper (Abstr., 1902, ii, 446). J. C. P.

A Periodic Contact Catalysis. GEORG BREDIG and J. WEINMAYR (*Zeit. physikal. Chem.*, 1903, 42, 601—611).—The rate of decomposition of hydrogen peroxide in contact with a mercury surface is periodic, and alternately rises and falls during the progress of the decomposition. The periodicity is indeed evident without special quantitative examination; if 10 c.c. of a 10—11 per cent. solution of pure hydrogen peroxide are poured on the top of a few c.c. of mercury in a carefully cleaned test-tube, the mercury becomes covered with a bright reflecting film of a bronze-like colour; as the catalysis of the hydrogen peroxide begins, this bright surface is obscured by the ascending gas bubbles, but from time to time it is again visible as the current of gas bubbles slackens for a while; this rhythmic process may go on for half an hour or an hour. The number of 'chemical vibrations' per minute varies considerably according to the conditions, and in such a case as the foregoing lies between 1 and 20; the number is increased by rise of temperature. The periodic character of the cata-

lysis is altogether hidden by the addition of certain substances (acids, alkalis, sodium sulphate and carbonate, potassium nitrate, chlorate, chloride, and bromide), some of which retard, whilst the others promote, the decomposition.

It has further been observed that the oscillations in the rate of chemical decomposition are accompanied by oscillations in the potential difference at the electrode $\text{H}_2\text{O}_2 \mid \text{Hg}$. Thus the cell



had an *E.M.F.* of 0.254 volt when the hydrogen peroxide electrode was active, and 0.322 volt when it was inactive (compare Brauer's experiments with chromium, *Abstr.*, 1901, ii, 635). In the above combination, the calomel electrode is the anode.

As might be expected from these electrical results, there is also a connection between the rate of catalysis and the surface tension of the mercury. Thus the mercury surface is flattened when the period of inactivity begins, whilst the curvature is apparently increased when the period of activity begins.

Further, it is possible by a slight mechanical shock to introduce a short period of inactivity, with the simultaneous appearance of the bronze-like surface. Nernst has shown that the potential at polarisable electrodes is especially sensitive to mechanical shock, and thus it seems from the foregoing observation that for the introduction of the inactive period, the polarisability of the catalytic mercury surface is of fundamental consequence.

In order that the 'chemical vibrations' may be well defined, it is necessary that the bronze-like reflecting film be formed on the mercury uniformly and simultaneously. It is possible that the film is periodically formed and broken in presence of hydrogen peroxide and mercury, but whether the film breaks just at the moment of initial activity could not be definitely decided. Periodic catalysis seems to take place only in the presence of the film, which probably consists of mercuric oxide; it is shown that ordinary yellow mercuric oxide is reduced by a 10 per cent. hydrogen peroxide solution with evolution of oxygen.

J. C. P.

Discoverer of Discontinuities in Solubility Curves. WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1903, 42, 501—502).—In reference to a discussion in Ostwald's *Lehrbuch* of the discovery of discontinuities in solubility curves and of the interpretation of these discontinuities relatively to the solution and the solid substance present, the author points out that as early as 1840 Kopp stated clearly that each substance must have its own solubility curve: he admits, however, that Kopp assumed a change to take place also in the solution at the point of section of the two solubility curves.

J. C. P.

Theory of Solubility Curves. WILHELM OSTWALD (*Zeit. physikal. Chem.*, 1903, 42, 503—504).—In reply to Meyerhoffer (preceding abstract), the author emphasises the advance made in recent years to the view that where two solubility curves cut each other the solid

substance ('Bodenkörper') alone undergoes sudden change. It is further pointed out that Gay-Lussac, not Kopp, was the discoverer of these discontinuities in solubility curves. J. C. P.

Position of Uranium in the Periodic System. WILLIAM ŒCHSNER DE CONINCK (*Chem. Centr.*, 1903, i, 375; from *Rev. gén. Chim. pure et appl.*, 5, 377—379).—The metallic character of uranium established by Pélilot, Zimmerman, and Moissan, and its analogies to tungsten and molybdenum, justify its position in the periodic system in proximity to iron and the metals of the iron group. E. W. W.

Saponin Froth. JAN VON ZAWIDZKI (*Zeit. physikal. Chem.*, 1903, 42, 612—616. Compare *Abstr.*, 1900, ii, 713).—When an aqueous solution of saponin is made to froth, the concentration of the saponin is greater in the froth than in the body of the solution. This has been shown by determining the index of refraction, which increases proportionally to the amount of saponin present in the solutions.

J. C. P.

Manometer with Zero-adjustment. ALFRED WOHL (*Ber.*, 1903, 36, 674—676).—The manometer is fitted with a pointer to which the mercury level is adjusted, and a vernier device similar to that of a barometer is provided for accurate reading. T. M. L.

Inorganic Chemistry.

Hydrogen Peroxide. K. BORNEMANN (*Zeit. anorg. Chem.*, 1903, 34, 1—42).—An historical account of the views which have been held as to the constitution and mode of formation of hydrogen peroxide is given. The method of Glaser (*Abstr.*, 1899, ii, 78) and Bose (*Abstr.*, 1899, ii, 348) of determining changes of direction of the decomposition tension curve has been applied to $N/5$ sulphuric acid in the hope of finding the conditions of the formation of hydrogen peroxide. The changes in direction of the curves were not sufficiently marked to permit definite conclusions to be drawn from them.

Electrolysis of the same electrolyte was carried out at a constant potential, the electrodes being so arranged that they could be polarised. The anode was a platinised platinum plate, and as cathode a polished platinum plate was used; when a low potential was employed, the cathode was constructed of platinum wire gauze. The amount of hydrogen peroxide formed was determined by titration with potassium permanganate and the current was measured by an iodine voltameter (the quantity of iodine liberated being titrated with sodium thio-sulphate). The advantage gained by this is that the two solutions used in the titrations can be titrated against each other and from the

results the percentage current-yield of hydrogen peroxide can be easily calculated. Experiments were made with potentials varying from 0 to 0.77 volt. In no case was hydrogen peroxide found at the anode, but at the cathode hydrogen peroxide could always be detected. If the cathode be strongly heated so as to charge it with oxygen before use, a high current strength is obtained, but relatively little hydrogen peroxide is produced. If the platinum be prepared by cathodic polarisation, a quantitative current-yield of hydrogen peroxide can be obtained. The explanation offered for this is that a platinum electrode charged with oxygen exerts a greater catalytic influence on the decomposition of the hydrogen peroxide than an electrode free from oxygen. Between the potentials 0.77 and 1.08 volt (Wilsmore's oxygen potential), hydrogen peroxide is also formed, but its concentration diminishes as the potential rises. Hydrogen peroxide appears always to be formed when hydrogen, in contact with water and oxygen at atmospheric pressure, is present in such concentration that the equilibrium pressure is exceeded.

Platinised platinum was left in contact with water, *N*/10 sulphuric acid, and *N*/10 sodium hydroxide for about 3 months and with the same solutions to which hydrogen peroxide had been added. In those cases where no hydrogen peroxide was added, its presence could not be detected with titanous acid, but by means of zinc iodide the presence of an oxidising substance was proved; where hydrogen peroxide had been added, it was completely destroyed.

In the catalysis of a mixture of hydrogen and oxygen by platinum, hydrogen peroxide is produced provided that the products of reaction are quickly removed from contact with the catalyser. But in an explosive mixture of these gases the equilibrium concentration of hydrogen peroxide lies outside the limit of its detection.

In the theoretical discussion, the author considers the equilibrium relationships between hydrogen peroxide, hydrogen, and oxygen on the one hand, and between H_2O_2 , H_2O , and $\frac{1}{2}\text{O}_2$ on the other. In agreement with the results obtained by Haber (Abstr., 1902, ii, 192) and by Luther (Abstr., 1901, ii, 301), it is proved that hydrogen peroxide must have two characteristic potentials at 0.8 volt and at 1.4 volts. The former of these is obtained at an electrode charged with hydrogen peroxide and hydrogen, the latter when the electrode is charged with hydrogen peroxide and oxygen. The equilibrium relationships, however, are not sufficient to explain the chemical and electrochemical behaviour of hydrogen peroxide; velocity phenomena must also be considered, and by means of these an explanation is offered why no anodic formation of hydrogen peroxide is possible.

J. McC.

Catalysis of Hydrogen Peroxide by Iodine Ions. GEORG BREDIG and J. H. WALTON, jun. (*Zeit. Elektrochem.*, 1903, 9, 114—119).—The velocity of decomposition of hydrogen peroxide in presence of an iodide is proportional to its concentration and to that of the iodine ions. The latter was found true for solutions of sodium and potassium iodide, cadmium iodide, of iodine and potassium iodide, and of potassium mercuric iodide.

The presence of free alkali diminishes the rate of decomposition. Potassium iodate has no effect on it and it is not itself reduced; potassium periodate is reduced at once to iodate. The alkaline reaction of a solution of potassium iodide and hydrogen peroxide points to the formation of hypoiodite. It can be formed, however, only in very minute quantities, because the conductivity of a solution of potassium iodide is almost unchanged when hydrogen peroxide is added to it. The decomposition of hydrogen peroxide is therefore probably due to the following reactions; $\text{H}_2\text{O}_2 + \text{I}' = \text{H}_2\text{O} + \text{IO}'$ and $\text{H}_2\text{O}_2 + \text{IO}' = \text{H}_2\text{O} + \text{O}_2 + \text{I}'$. The second reaction takes place instantaneously, so that it is only the velocity of the first which is measured. T. E.

A Probable Cause of the Different Colours of Iodine Solutions. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1903, 25, 50—55).—Krüss and Thiele (Abstr., 1894, ii, 445) have attempted to discover some relationship between the colour of iodine solutions and the chemical nature of the solvent. By molecular weight determinations of dilute solutions, they concluded that the iodine molecule consisted of two atoms; concentrated solutions, on the other hand, gave high molecular weights, although the association thus indicated was not accompanied by any colour change.

The author finds that a simple connection exists between the colour of iodine solutions and the chemical behaviour of the solvent, a connection which had not previously been noted because the solvents were not of sufficient purity. When pure solvents are employed, the colour of their iodine solutions is either violet or brown. Violet solutions result with hydrocarbons, halogen compounds (not iodides), nitro-compounds, and carbon disulphide, whilst brown solutions are formed from iodides, alcohols, ethers, ketones, acids, and esters, nitriles, nitrilobases, and various sulphur compounds. The recent work of Baeyer and Villiger on the basic properties of oxygen leads the author to assume that additive compounds (solvent-molecule + I_2) are formed in all brown iodine solutions. The violet solutions are supposed to contain simple iodine molecules. Brown solutions tend to become violet when heated and violet solutions brown when sufficiently cooled.

A. McK.

Combustion in Gaseous Mixtures other than Air. LOUIS PELET and P. JOMINI (*Bull. Soc. chim.*, 1903, iii, 29, 197—201. Compare this vol., ii, 130).—When an organic substance is burnt in a determinate volume of a gas mixture containing oxygen, the flame is not extinguished, even in presence of 75 per cent. of carbon dioxide in the gaseous products of combustion, so long as the latter contain a certain minimum proportion of oxygen; this proportion depends on the nature of the combustible, and for each substance it varies within narrow limits with the conditions of the experiment, thus for alcohol the minimum varies from 12 to 15.3 and for coal gas from 10.7 to 12.5 per cent. It was observed that in burning substances containing both carbon and hydrogen the combustion of the former, but not that of the latter, was occasionally inhibited by the presence of the carbon dioxide.

The experimental results from which these conclusions were drawn are tabulated in the original. T. A. H.

Amorphous Sulphur. I. Influence of Amorphous Sulphur on the Freezing Point of Liquid Sulphur. ALEXANDER SMITH and WILLIS B. HOLMES (*Zeit. physikal. Chem.*, 1903, 42, 469—480).—Details are given of work already published in outline (see this vol., ii, 139). It is shown that mixtures of soluble sulphur and amorphous sulphur (up to 5 per cent.) may be analysed by extraction with carbon disulphide; the allowance to be made for the slight solubility of the amorphous form in this solvent has been determined by the authors for mixtures of different composition. The foregoing method has been used to analyse mixtures of soluble and amorphous sulphur after determination of the freezing point, and it is shown that there is no appreciable displacement of the equilibrium between the two forms during either the determination of the freezing point or the subsequent cooling.

As previously indicated, the relationship between the freezing point of sulphur and the amount of the amorphous form present is a linear one, and the straight line in question, if produced, cuts the temperature axis at 119.25° , which is therefore the freezing point of pure monoclinic sulphur. This has been confirmed by the observation that two samples, consisting practically of pure soluble sulphur, solidified at 119.165° and 119.17° respectively. J. C. P.

Preparation of Hydrogen Sulphide in the Dry Way. E. PROTHIÈRE (*Chem. Centr.*, 1903, i, 492; from *L'Union pharmac.*, 1902, No. 12).—Hydrogen sulphide may be prepared by heating a mixture of 30 grams of vaselin with 70 of sulphur; from such a mixture, 48.18 litres of gas may be obtained. E. W. W.

Compounds of Sulphur Dioxide with Salts. PAUL WALDEN and M. CENTNERSZWER (*Zeit. physikal. Chem.*, 1903, 42, 432—468. Compare Abstr., 1902, ii, 245).—The evidence in favour of the existence of these compounds is discussed (compare Péchard, Abstr., 1900, ii, 398; Berg, Abstr., 1900, ii, 535; Volhard, Abstr., 1900, ii, 650; Fox, Abstr., 1902, ii, 645).

When small quantities of the dry salts, potassium, sodium, ammonium, tetramethylammonium, and trimethylsulphonium iodides, ammonium, sodium, and potassium thiocyanates, were placed in flasks and submitted to a current of sulphur dioxide, the only two that showed any marked change of appearance or increase of weight were trimethylsulphonium iodide and potassium thiocyanate, probably because the compounds formed are, in most cases, unstable at the ordinary temperature.

For experiments at lower temperatures, potassium iodide was chosen, and it was observed that from a 20 per cent. solution of potassium iodide in sulphur dioxide, which was liquid at the ordinary temperature, well-formed red crystals separated on cooling in a mixture of snow and salt; some of these crystals were freed from mother liquor as far as possible at a low temperature and analysed by expulsion of the sulphur dioxide; the analyses pointed to the formula KI_4SO_2 for

these crystals. The proof of the existence of such a compound was completed by a study of the freezing point curve for mixtures of potassium iodide and sulphur dioxide. Sulphur dioxide freezes at -72.7° , and the addition of 0.34 molecular per cent. of the iodide lowers the freezing point slightly to a eutectic point. From solutions containing from 0.34 to about 8 molecular per cent. of potassium iodide, a yellow, crystalline powder separates on cooling, and the freezing point curve shows a maximum at about -23.4° , corresponding with this substance. This maximum is followed by a second eutectic point, and then a further rise in the curve, during which red crystals are deposited on cooling. This branch of the curve ends at the point corresponding with the compound KI_4SO_2 , which has the freezing point $+0.26^{\circ}$. Analysis pointed to the above-mentioned yellow crystals having the formula KI_4SO_2 .

An unsuccessful attempt was made to establish the existence of the compound KI_4SO_2 by measurement of vapour pressure.

As described before (*loc. cit.*), some sulphur dioxide salt solutions deposit solid on heating to a point below the critical temperature. A solution of potassium iodide of medium concentration separates into two layers on heating, and, on further heating, well-formed, yellow crystals are deposited, and one of the liquid phases disappears; on cooling, the corresponding reverse changes are observed. From the phase rule, it follows that the temperature at which the solid phase is in equilibrium with the two liquid phases must be independent of the concentration; this temperature is 88.1° . Dilute and concentrated solutions of potassium iodide deposit solid on heating without the intermediate formation of two liquid phases.

Comparison of the freezing points of aqueous solutions containing both sulphur dioxide and potassium iodide (or thiocyanate) with those of solutions of sulphur dioxide and potassium iodide (or thiocyanate) separately shows that there are probably compounds formed which, however, are dissociated to a large extent. Further, in agreement with Fox's results (*loc. cit.*), sulphur dioxide is more soluble in aqueous solutions of potassium chloride, bromide, iodide, and thiocyanate, rubidium and tetramethylammonium iodides, and resorcinol than in pure water; in sodium chloride solutions, sulphur dioxide is less soluble.

Sulphur dioxide is compared with the two well-known ionising solvents, water and ammonia, in its tendency to form complexes. The existence of these complexes, however, in sulphur dioxide solutions will not account for the deviations from the requirements of the osmotic theory exhibited by these solutions.

J. C. P.

Hyposulphurous Acid. JULIUS MEYER (*Zeit. anorg. Chem.*, 1903, 34, 43—61).—An attempt to prepare sodium hyposulphite by electrolysis of sodium hydrogen sulphite failed. The hyposulphite is actually formed because the liquid acquires the characteristic reducing properties of sodium hyposulphite, but the concentration cannot be sufficiently increased to allow of isolation of the salt.

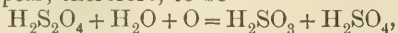
The salt used in the investigation was crystallised from water by saturating at $25-30^{\circ}$ in an atmosphere of carbon dioxide and then separating the solid by cooling in a freezing mixture. Bernthsen's

analysis (Abstr., 1900, ii, 203) of the sodium salt, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, has been confirmed by determination of the sodium and sulphur. The amount of oxygen absorbed from copper sulphate is also in agreement with Bernthsen's formula, and contradicts that of Schützenberger. The depression of the freezing point of water containing the salt indicates that the formula is $\text{Na}_2\text{S}_2\text{O}_4$, but, on account of decomposition, the basicity of the acid could not be determined by the Ostwald and Walden rule from the conductivity.

Several reducing actions of sodium hyposulphite have been studied. With potassium nitrite in alkaline solution, no reaction whatever takes place, but if the air has access to the mixture the hyposulphite is oxidised, and the sodium hydrogen sulphite produced acts on the potassium nitrite with formation of potassium amidosulphonate: $\text{KNO}_2 + 3\text{NaHSO}_3 + \text{H}_2\text{O} = \text{NH}_2 \cdot \text{SO}_3\text{K} + \text{NaOH} + 2\text{NaHSO}_4$. In acid solution, reduction takes place and nitrous oxide (mixed with nitrogen?) is evolved.

Ammoniacal copper sulphate loses its blue colour with hyposulphite, and if excess of the reducing agent is added the solution assumes a yellow tinge; this yellow colour is not due to the presence of copper hydride, as has been assumed, but to free hyposulphurous acid produced by the action of the sodium hydrogen sulphite on the excess of sodium hyposulphite: $\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{NaHSO}_3$; $2\text{NaHSO}_3 + \text{Na}_2\text{S}_2\text{O}_4 = 2\text{H}_2\text{S}_2\text{O}_4 + 2\text{Na}_2\text{SO}_3$. In dilute solution, the free acid is stable for some time in presence of cuprous salts, but in concentrated solution reduction to metallic copper quickly takes place. If a very dilute solution of copper sulphate be employed, a colloidal solution of copper is obtained. Colloidal solutions of silver, mercury, bismuth, and selenium can also be obtained by reduction with hyposulphite. With dilute platinic chloride solution, a darkening is observed, but it is doubtful if a pseudo-solution is formed, because addition of electrolytes or heating does not cause separation of metallic platinum in the solid condition.

With ammoniacal copper sulphate, sodium hyposulphite is oxidised to sulphite according to the equation: $\text{Na}_2\text{S}_2\text{O}_4 + \text{CuSO}_4 + 2\text{H}_2\text{O} = 2\text{NaHSO}_3 + \text{Cu}_2\text{SO}_4 + \text{H}_2\text{SO}_4$. Under special conditions, the products of oxidation are sulphuric acid, dithionic acid, and thiosulphuric acid. Thus, with hydrogen peroxide, almost all the sulphur appears in the form of sulphuric acid, but a small quantity is transformed into dithionic acid. Schützenberger has stated that on shaking sodium hyposulphite solution with air, double the amount of oxygen necessary for the formation of sodium hydrogen sulphite is absorbed; this has not been confirmed, although more oxygen is absorbed than is indicated by the equation: $2\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{NaHSO}_3$. The excess of oxygen absorbed has been attributed to the formation of hydrogen peroxide or of a hyposulphite peroxide (Engler, Abstr., 1900, i, 399). These views, however, cannot be confirmed, and it seems probable from the amount of sulphate always formed that the excess of oxygen is used in carrying the oxidation past the state of sulphurous acid. The reactions taking place when sodium hyposulphite is shaken with oxygen would appear, therefore, to be



and, to a small extent, $2\text{H}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{H}_2\text{SO}_3$.

It has not been possible to obtain salts of hyposulphurous acid other than those of the alkali and alkaline earth metals, and even these are not stable, but decompose spontaneously with production of much thiosulphate. The decomposition takes place also in dilute solution; at the ordinary temperature, it is slow, at 45° it is observable, and at the boiling point it takes place quite quickly. Solutions of sodium hyposulphite were heated at 45°, 60°, and 80° respectively for definite times, and the diminution of reducing power was determined by estimating the amount of oxygen absorbed. The results, graphically represented, show that the decomposition starts slowly, rises to a maximum velocity, then again becomes retarded. Part of the products of the decomposition react on still undecomposed salt, and consequently the velocity of decomposition is proportional both to the extent of decomposition and to the quantity of salt left undecomposed. The decomposition on heating is probably to be represented by the equation $2\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaHSO}_3$.

When a solution of sodium hyposulphite is acidified, it becomes yellow or orange-coloured, and much sulphur is separated; at the same time, sulphur dioxide is evolved. As no polythionic acids are formed (Bernthsen, *Annalen*, 1881, 208, 148) during the decomposition, the sulphur must be formed from thiosulphuric acid or from hydrogen sulphide and sulphur dioxide.

J. McC.

Odour of Heated Selenium. BERNHARD RATHKE (*Ber.*, 1903, 36, 600).—The characteristic radish-like odour of selenium when heated on charcoal in the blowpipe is due to carbon diselenide and not to a suboxide of selenium.

T. M. L.

Selenium Sulphide. BERNHARD RATHKE (*Ber.*, 1903, 36, 594—599).—In spite of their variable composition, the author maintains that the crystals formed by fusing together selenium and sulphur and crystallising the product from carbon disulphide contain a definite sulphide of selenium. (1) Unlike free selenium, the product is not rendered insoluble in carbon disulphide by heating at 100°. (2) In spite of their very great difference in solubility, selenium and sulphur cannot be separated from the product by fractional crystallisation. (3) The solubility of the selenium in this condition is several times as great as when uncombined (compare Ringer, *Abstr.*, 1902, ii, 651).

T. M. L.

Electrolytic Preparation of Hydroxylamine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 133457).—Nitric acid may be reduced to hydroxylamine by electrolysis in sulphuric acid solution. The electrolysing vessel is divided by a porous partition and contains 50 per cent. sulphuric acid in both compartments. The cathode is amalgamated lead, the anode lead; 50 per cent. nitric acid is added drop by drop to the cathode compartment and during the passage of the current the temperature maintained by cooling coils below 20°. A current density of 60—120 amperes per sq. dm. is suitable. The hydroxylamine is isolated from the solution by the usual methods (compare Tafel, *Abstr.*, 1902, ii, 559).

C. H. D.

Solubility of Boric Acid in Acids. W. HERZ (*Zeit. anorg. Chem.*, 1903, 34, 205—206).—The solubility was determined by shaking solid boric acid with solutions of acids of known strength at 26° and determining the total acidity by titration. The following results give the normality of the acid solution used and of the dissolved boric acid :

H ⁺ .	B(OH) ₃ .	H ⁺ .	B(OH) ₃ .
In sulphuric acid :		In nitric acid :	
0.548	0.746	0.241	0.818
2.74	0.518	1.206	0.676
5.48	0.312	1.607	0.593
8.75	0.092	2.411	0.567
		5.96	0.268
		7.38	0.238
In tartaric acid :		In acetic acid :	
0.955	0.890		
1.909	0.923		
2.51	0.962	0.570	0.887
3.316	1.07	2.85	0.538
		5.70	0.268

The solubility in tartaric acid solution appears somewhat high, but this is due to the formation of complex molecules. J. McC.

Preparation of Carbon Monosulphide, CS. JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1903, 34, 187—193).—The author gives an account of the attempts which have been made to prepare carbon monosulphide. He concludes that since carbon monosulphide is an endothermic substance, like carbon disulphide, the most probable method of forming it will be by decomposing the disulphide at a high temperature. This has been effected by repeatedly passing a current of nitrogen saturated at the ordinary temperature with carbon disulphide vapour over heated copper. Starting with 87 c.c. of nitrogen, which on saturation with carbon disulphide gave 140 c.c. of gas, it was found that by passing the mixture over heated copper seven times, the volume increased to 192 c.c. Thirty-four c.c. of this gas were then passed repeatedly over hot copper, and finally 82 c.c. of gas were obtained, or, if the whole of the mixture had been treated, 463 c.c. would have been obtained. Thus 376 c.c. of gas were formed (there being 87 c.c. of nitrogen). The proportion of gas to nitrogen was, therefore, 4.3 : 1. In another experiment, the proportion was 4.2. It is assumed that no substance other than carbon monosulphide could have been formed, and the result obtained by exploding the gas mixture with oxygen, and then sparking in order to combine the nitrogen with oxygen, was in agreement with the assumption that carbon monosulphide and nitrogen were present in the proportion of about 4 to 1. J. McC.

Melting of Quartz in the Electric Furnace. R. S. HUTTON (*Chem. Centr.*, 1903, i, 431; from *Amer. Electrochem. Soc.*, 1902, reprint).—The original paper contains a description and a diagram of an electric furnace of the Moissan type adapted for the melting of quartz. The reduction of the quartz by the carbon is prevented by employing an oxidising atmosphere. Satisfactory results were obtained with graphite moulds (for capillary tubes) and with a carbon crucible. When pure sand was melted in the furnace, the product was less transparent, but prolonged heating at a high temperature tended to remove the bubbles.
E. W. W.

The Displacement of the Sulphuric Acid of Alkali Hydrogen Sulphates by Water. ALBERT COLSON (*Compt. rend.*, 1903, 136, 366—368).—The temperature at which water can be added to a solution of a substance without causing alteration of the temperature is called the "dead point" and gives an indication when addition of water does not effect a chemical change. Four solutions have been investigated: *A*, a solution of sodium sulphate (142 grams) in 98 per cent. sulphuric acid (1000 c.c.); *A*₁, a mixture of equal volumes of solution *A* and water; *B*, a solution of potassium hydrogen sulphate in 4 parts of water; *B*₁, a mixture of equal volumes of solution *B* and water. The "dead point" of the dilution of *A* lies between 16° and 17°; of *A*₁ at 8°; of *B* at 14°; and of *B*₁ at -2°. From these results, the conclusion is drawn that the alkali hydrogen sulphates are decomposed by water into alkali sulphate and sulphuric acid. A solution of potassium hydrogen sulphate behaves as a freshly prepared solution of potassium sulphate and sulphuric acid, and on slowly cooling deposits crystals of the normal sulphate.
K. J. P. O.

Decomposition of Dissolved Sodium Carbonate into Sodium Hydroxide and Carbon Dioxide. FRIEDRICH W. KÜSTER and MAX GRÜTERS (*Ber.*, 1903, 36, 748—752).—When an *N*-solution of sodium carbonate is boiled in a silver reflux apparatus, it gradually and continuously loses carbon dioxide, and the amount of the latter evolved can be determined by carrying it off in a stream of mixed oxygen and hydrogen and absorbing it in standard baryta solution; the quantity of carbon dioxide lost in each hour is approximately inversely proportional to the amount of sodium hydroxide in the solution. After 38 hours, only 83·8 per cent. of the normal alkali is carbonate, the remainder being hydroxide.

At 50°, practically no carbon dioxide is evolved from a normal solution of the carbonate in 17 days, but at 90° it is given off slowly and uniformly, so that after 358 hours 1·70 per cent. of the alkali is transformed into hydroxide; the measurements given show that its vapour pressure at this temperature is 0·000072 atmospheres or 0·055 mm. Even normal solutions containing 90 equivalents per cent. of carbonate and 10 equivalents per cent. of hydroxide lose carbon dioxide very slowly at 90°, the partial pressure being 0·019 mm.

W. A. D.

Solubility of Ammonium Nitrate in Water between 12° and 40°. WOLF MÜLLER and PAUL KAUFMANN (*Zeit. physikal. Chem.*, 1903, 42, 497—500).—For the solubility of ammonium nitrate, Schwarz found a smaller value at 36° than at 35°, and in view of this unlikely result the authors have carefully traced the solubility curve of this substance between 12° and 40°. They find a discontinuity (1) in the solubility curve, (2) in the density-temperature curve for the saturated solutions—in both cases at 32°; otherwise the curves are perfectly regular. The temperature of 32° is the transition point of the rhombic I and rhombic II forms of ammonium nitrate (compare Müller, *Abstr.*, 1900, ii, 188). J. C. P.

Action of Hydrogen on Silver Sulphide in Presence of Antimony Trisulphide and of Arsenic Trisulphide. HENRI PÉLABON (*Compt. rend.*, 1903, 136, 454—456).—The ratio of the partial pressure of hydrogen sulphide to the total pressure of the gaseous mixture was determined when hydrogen was heated in contact with silver sulphide, mixed either with antimony trisulphide or arsenic trisulphide at constant temperature. The following values of the ratio (R) were found when hydrogen was heated at 635° with 0.5 gram of antimony trisulphide mixed with the quantity of silver sulphide given :

Weight of silver sulphide.	R .
0.35 gram	0.617
0.40 "	0.610
0.50 "	0.593
0.60 "	0.551
0.70 "	0.528
0.80 "	0.518

The value of R increases with an increasing proportion of antimony sulphide in the mixture. This result is a consequence of the fact that the dissolved silver sulphide diminishes the vapour pressure of the antimony sulphide and this causes a decrease of the partial pressure of the hydrogen sulphide. When these results are represented graphically, points of inflexion are noticed at the parts of the curve corresponding with the mixtures Sb_2S_3 , Ag_2S and Sb_2S_3 , $2\text{Ag}_2\text{S}$.

Similar results were obtained with arsenic trisulphide at 630°. 0.5 gram of arsenic sulphide was used :

Weight of silver sulphide.	R .
1.0 gram	0.941
1.5 "	0.875
2.0 "	0.825
3.0 "	0.772
4.0 "	0.743
5.0 "	0.735

J. McC.

Ammonio-Silver Compounds in Solution. WILLIS R. WHITNEY and ARTHUR C. MELCHER (*J. Amer. Chem. Soc.*, 1903, 25, 69—83).—From the work of Konowaloff, Bodländer, and others, it has been

rendered probable that, in dilute solutions of ammonio-silver compounds, the silver exists almost entirely as the complex cathion $\text{Ag}(\text{NH}_3)_2^+$. This conclusion has now been confirmed by the method of electric transference. When an electric current is passed from a solution containing ammonia and silver nitrate into an adjoining solution of a normal sodium salt, the silver migrates as a complex ion into the latter solution. A similar result is attained when silver sulphate is substituted for silver nitrate, the ion in both cases being supposed to have the formula $\text{Ag}_n(\text{NH}_3)_{2n}$.

The addition of silver oxide to ammonia solutions does not alter their freezing points. Ammonio-silver hydroxide may be formulated $\text{Ag}_n(\text{NH}_3)_{n+1}(\text{OH})_n$; it is shown to be a highly dissociated base, and its equivalent conductivity changes only very slightly with increasing dilution. Solubility determinations of silver oxide, chloride, and bromide respectively were made in aqueous ammonia solutions. Within the limits of concentration in the experiments, the amount of silver oxide dissolved was almost exactly proportional to the quantity of ammonia in solution. In the case of silver chloride, the ratio $C_{\text{NH}_3} : C_{\text{Ag}}$ varied continuously, but approximated to a constant, 20.2, in dilute solution. With silver bromide, where the concentration of the dissolved silver is small, the ratio shows no progressive variation with the concentration of the ammonia; the solubility is proportional to the concentration of the ammonia. The ratio of the solubilities in dilute ammonia of silver oxide and chloride is the same as the ratio of their solubilities in water. The solubility of silver oxide in ammonia is much greater at 0° than at 25° , whilst the reverse is the case for its solubility in pure water; this is due to a much slighter dissociation-tendency of the complex ion at the lower temperature.

A. McK.

Formation of Bleaching Powder. F. WINTELER (*Zeit. angew. Chem.*, 1903, 16, 32—34).—A criticism of the work of Foerster and Müller (Abstr., 1902, ii, 640, 642; and this vol., ii, 142) and of Foerster and Jorre (Abstr., 1900, ii, 242) on hypochlorous acid and its conversion into chloric and hydrochloric acids.

K. J. P. O.

Solubility of Gypsum in Solutions of Sodium Chloride. CHARLES CLOEZ (*Bull. Soc. chim.*, 1903, [iii], 29, 167—169).—The solubility of calcium sulphate in aqueous solutions of sodium chloride increases with the concentration of the latter salt (compare Ditte, Abstr., 1898, ii, 510). This accounts for the observation that solutions containing both sodium chloride and calcium sulphate deposit on evaporation, first, pure sodium chloride, and eventually, a mixture of the two salts.

The removal of magnesium sulphate from brine, intended for conversion into table salt, by addition of lime is objectionable, since a portion of the calcium sulphate produced remains in the product. The solubilities of calcium sulphate in solutions of sodium chloride of various strengths are tabulated in the original.

T. A. H.

Plaster of Paris. I. Dehydration of Gypsum. CHARLES CLOEZ (*Bull. Soc. chim.*, 1902, [iii], 29, 169—171).—Gypsum is completely dehydrated when heated for 4 hours at 145° (compare Lacroix, *Compt. rend.*, 1898, 126, 360, and 553); the product is hygroscopic, and when exposed to air at the ordinary temperature (14 — 16°) absorbs in the first hour 3.7 per cent., and in 19 hours 7.5 per cent., of water; beyond this point, absorption is slow, and after 78 hours only amounts to 7.93 per cent. (compare Landrin, *Abstr.*, 1875, 106). When exposed to air at lower temperatures (5 — 7°), the absorption is slower, but of the same order. The amount of water absorbed, 7.8 per cent., does not correspond with the formation of a definite hydrate. Curves showing the rate of absorption at the temperatures mentioned are given in the original.

T. A. H.

Plaster of Paris. II. "Setting." CHARLES CLOEZ (*Bull. Soc. chim.*, 1903, [iii], 29, 171—174).—Anhydrous calcium sulphate, when placed in its own weight of water, raises the temperature of the latter by 14° to 22° ; the temperature afterwards falls steadily for about 10 minutes, then remains stationary for a short time, and finally rises to a higher level than the temperature produced immediately on admixture. Similar, but less marked, changes occur when partially dehydrated gypsum is placed in water. The temperature changes in the order indicated are regarded as due to hydration, solution of the hydrate formed, and "setting" of the supersaturated solution produced (compare Le Chatelier, *Abstr.*, 1883, 712).

T. A. H.

Tetragenic Double Salts, with Particular Reference to Kainite. WILLY MEYERHOFFER (*Zeit. anorg. Chem.*, 1903, 34, 145—173).—A tetragenic double salt is one containing four different elements or radicles (exclusive of water of crystallisation), such as kainite, $\text{MgSO}_4\cdot\text{KCl}\cdot 3\text{H}_2\text{O}$. If the solution of such a salt is neutral, determination of three of the components is sufficient to settle the composition. It is deduced that a tetragenic double salt must have at least two temperatures of formation and may have three. The temperatures of formation of kainite are 76° and 85° . Although the composition of a solution may not be known, certain relationships between the composition and the nature of the solid with which it is in contact can be derived. These relationships are termed the "characteristics" of the solution, and they are illustrated in the case of kainite and some other salts.

The polytherms, or equilibrium relationships at different temperatures, of kainite are discussed for the whole range of existence of this substance, and it is proved that besides the above primary temperatures of formation others of a secondary nature, lower than these, must exist. It is shown that kainite can best be represented by the formula $\text{MgSO}_4\cdot\text{KCl}\cdot 3\text{H}_2\text{O}$, and not by $\text{MgSO}_4\cdot\text{K}_2\text{SO}_4\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$.

In a discussion of the natural formation of the "hard salt" bed at Stassfurt, it is proved that at any rate in all cases the formation has not taken place by rapid washing away of liquor from carnallite and kieserite so as to leave no time for the formation of kainite.

The author discusses the technical processes in use for preparing

other salts from kainite, and considers the methods of Douglas, of Precht, and of the Westregeln works from the standpoint of the doctrine of equilibrium. J. McC.

Determination of the Solubility of Magnesium Oxide and Zinc Oxide in Water. DUPRÉ, jun., and BIALAS (*Zeit. angew. Chem.*, 1903, 16, 54—55).—The authors have determined the solubility in water of magnesium and zinc oxides by means of the electric conductivity of their solutions. Kohlrausch's telephone method was used with a slight modification in the electrical arrangements, for which the original article and drawings should be consulted.

From the results, it has been established that the solubility in water at 18° of magnesium oxide is 1 in 172,000; that of zinc oxide, 1 in 236,000. L. DE K.

Determination of Boiling Points of Copper and Zinc. CH. FÉRY (*Ann. Chim. Phys.*, 1903, [vii], 28, 428—432. Compare this vol., ii, 124).—Both zinc and copper can be readily distilled by the aid of an electric furnace. The boiling point of the zinc, measured by a thermoelectric junction (compare *loc. cit.*), was 1040°, and is probably about 100° too high. The boiling point of copper was found to be 2100°. It was found possible to completely separate the two metals from an alloy by fractional distillation. K. J. P. O.

Copper Cadmium Alloys. P. DENSO (*Zeit. Elektrochem.*, 1903, 9, 135—137).—Alloys of copper and cadmium containing less than 10 per cent. of copper are treated with cold 5 per cent. hydrochloric acid, or are used as anodes in a neutral solution of cadmium sulphate. Cadmium is dissolved, and crystals of an alloy having the composition CuCd_3 are left behind. T. E.

Some Products of Reduction of Copper Salts by Hydroxylamine. E. PÉCHARD (*Compt. rend.*, 1903, 136, 504—506).—*Cuprous acetate*, $\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_2$, is obtained in white, needle-shaped crystals by slowly adding a solution of hydroxylamine sulphate to a warm solution of cupric acetate containing excess of ammonium acetate. When the solution is completely decolorised, acetic acid is added and the cuprous acetate deposits. It is very easily oxidised in the air. It is partially decomposed by water into cuprous oxide and acetic acid, but it is stable in presence of acetic acid.

Ammonio-cuprous sulphate, $\text{Cu}_2\text{SO}_4 \cdot 4\text{NH}_3$, is precipitated when hydroxylamine sulphate is added to an alcoholic ammoniacal solution of cupric sulphate, but the precipitate also contains much ammonium sulphate. It can be prepared pure by reducing a suspension of basic cupric carbonate in dilute ammonia solution with hydroxylamine sulphate at 80°. Carbon dioxide, nitrogen, and nitrous oxide are evolved. To the cooled solution, alcohol is added, and a heavy white precipitate of ammonio-cuprous sulphate is formed. It is readily oxidised in the air and soluble in ammonia solution, but is decomposed by pure water. When heated at 100°, it does not lose ammonia, but above

this temperature it loses ammonia, and the cuprous sulphate residue decomposes.

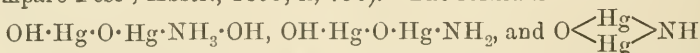
Other cuprous salts of acids containing oxygen can be produced by this process. J. McC.

Existence of Electrolytic Peroxides of Lead, Nickel, and Bismuth. AUGUSTE HOLLARD (*Compt. rend.*, 1903, 136, 229—231).—Up to the present, it has been supposed that the peroxide of lead, PbO_2 , is alone deposited on the anode during the electrolysis of a solution of a lead salt, and consequently the factor, 0.866, has been used to express the ratio of the quantity of lead used to the amount of oxide formed. It is now found that this factor is too large; an oxide of lead is therefore deposited which contains more oxygen than the dioxide; further, the proportion of this higher oxide is the greater the less the concentration of the lead in the solution. In the experiments, 300 c.c. of a solution of lead nitrate were used, containing quantities of lead varying from 0.0106 to 10 grams; some excess of nitric acid and copper nitrate corresponding with 10 grams of copper were also present. Platinised platinum gauze was used as anode. For the most dilute solution, the value of the factor was 0.740, and gradually rose to 0.861 for the most concentrated solution. It was not ascertained whether a single oxide or several higher oxides were formed. In the electrolysis of a moderately concentrated solution of a lead salt, lead dioxide is apparently at first deposited, and then becomes covered with a layer of a higher oxide as the amount of lead in the bath decreases.

When a solution of nickel (0.05 gram in 300 c.c.) containing chromic acid and alkali pyrophosphate is electrolysed at 70° , using a current of 0.1 ampere for 54 hours, the peroxide NiO_4 was deposited. On electrolysis of a solution of bismuth sulphate, 0.05 gram of bismuth for 300 c.c. containing excess of nitric acid and copper sulphate (40 grams), a peroxide, Bi_2O_7 , was deposited as a citron-yellow powder.

K. J. P. O.

Mercury Derivatives of Nitrogen Compounds. HUGO FÜRTH (*Monatsh.*, 1902, 23, 1147—1161).—That the action of ethyl iodide on the infusible, white precipitate obtained when a solution of mercuric chloride is treated with ammonia leads to the formation of mercuric iodide and ethylamine, and that ethylamine is also formed by the action of ethyl iodide on Millon's base, is evidence in favour of the formula $\text{NH}_2\cdot\text{HgCl}$ for the former compound (Hofmann and Marburg, *Abstr.*, 1899, i, 486), but against Rammelsberg's formula for the latter (compare Pesci, *Abstr.*, 1899, ii, 750). The formulæ



agree with the properties of Millon's base and its dehydration derivatives better than Hofmann and Marburg's formulæ.

Millon's base is precipitated from an aqueous solution of mercury acetamide on addition of ammonia; ammonium chloride precipitates the chloride, ammonium nitrate, the nitrate, of the base.

The action of aniline hydrochloride on excess of mercury acetamide

leads to the formation of the chloride of a *phenyl* derivative of Millon's base, $\text{HgCl} \cdot \text{O} \cdot \text{Hg} \cdot \text{NHPh}$, which is obtained as a yellow precipitate. Excess of aniline hydrochloride leads to the formation of the crystalline, phenylated, fusible, white precipitate described by Gmelin.

On addition of mercurous nitrate to mercury acetamide, a white precipitate, which turns yellowish-green, is formed. This substance is blackened by ammonia, gives off nitrous fumes when heated, is also formed by the action of mercuric oxide on mercurous nitrate in boiling aqueous solution, and has probably the constitution represented by the formula $\text{Hg} \cdot \text{O} \cdot \text{Hg} \cdot \text{NO}_3$. G. Y.

Revision of the Atomic Weight of Cerium. BOHUSLAV BRAUNER and ALEXANDER BATĚK (*Zeit. anorg. Chem.*, 1903, 34, 103—123).—The authors give a short account of the various determinations of the atomic weight of cerium which have been made up to the present. The cerium used in the investigation was obtained from Bastnäs and did not contain thorium. The oxalate was prepared in the usual way, and then boiled for a long time with potassium oxalate solution to remove the metals of the yttrium group. Basic cerium sulphate-nitrate was then precipitated and the precipitate dissolved in a mixture of nitric and sulphuric acids and the basic salt again precipitated. The salt was then treated with sulphur dioxide and sulphuric acid and the ceric sulphate thus obtained was subjected to fractional crystallisation at 40—50°. Cerium oxalate was prepared from the crystals and analysed. It was proved that cerium oxalate has a normal composition and is suitable for atomic weight determinations. The second method of purification adopted was that of Wyruboff and Verneuil, namely, by precipitation with hydrogen peroxide and ammonia. The third method consisted in forming the basic nitrate by hydrolysis and, after converting this into the nitrate, the ammonium nitrate double salt was prepared and recrystallised several times.

The atomic weight of cerium calculated from the analysis of the sulphate and oxalate is 140.249. The mean value from seven analyses of the sulphate is 140.21, and the mean value from 18 analyses of the oxalate is 140.265 ($\text{O} = 16$).

Incidentally it is mentioned that the purest cerium tetroxide which has been obtained is tinged slightly brown, and it has not been possible, by any modification of the process of preparation, to produce a colourless tetroxide as described by Wyruboff and Verneuil.

J. McC.

Revision of the Atomic Weight of Cerium. II. BOHUSLAV BRAUNER (*Zeit. anorg. Chem.*, 1903, 34, 207—237).—By fractional crystallisation, pure ceric sulphate has been obtained and also a pure ceric oxalate. The mean value for the atomic weight of cerium deduced from five determinations of the cerium tetroxide, obtained by igniting the oxalate, and four determinations of the oxalic radicle is 140.246. The oxalic acid was determined by adding a weighed quantity of potassium permanganate just insufficient to effect complete oxidation and finishing by titration with

N/10 potassium permanganate solution, of which less than 0.5 c.c. was required.

By the action of potassium iodide and hydrochloric acid in a sealed tube at 90° on cerium tetroxide, it has been proved that this substance has the formula Ce_2O_4 .

Octahydrated cerium sulphate does not lose its water of crystallisation completely at 250° as Wyruboff and Verneuil assert. The loss of water is not complete until a temperature of 630° is reached, and at 650° the sulphate begins to decompose with formation of an insoluble basic sulphate. The atomic weight deduced from the weight of cerium tetroxide obtained from octahydrated ceric sulphate by ignition is 140.25 and 140.26.

It has been noticed that the weight of cerium tetroxide increases with the time between the ignition and the weighing; this has been proved not to be due to the cooling or to the hygroscopic nature of the substance, but is best accounted for by assuming that a condensation or occlusion of gas (oxygen) takes place on the solid, and this is in conformity with the well-known catalytic oxygen-carrying power of the substance.

The author gives an account of the various descriptions of the colour of cerium tetroxide which have been given. In Sterba's process (Abstr., 1901, ii, 602), an absolutely white oxide is obtained, but this has now been proved to contain silver. A pure white oxide is produced by precipitating ceric hydroxide and treating this with chlorine in presence of excess of potassium hydroxide. The precipitate is dissolved in dilute sulphuric acid and the sulphate on ignition gives a white tetroxide; this, however, is not pure but contains silica. When the sulphate is prepared from either of these white tetroxides, its analysis leads to the atomic weight 140.248 for cerium. On ignition of the sulphate obtained from the white tetroxide, a tetroxide is obtained which has a yellow tinge. Pure cerium tetroxide has always this yellow tinge; if it is white, it must be regarded as impure. The author sets up the hypothesis that pure cerium tetroxide is white, but by condensation of oxygen on its surface it assumes a yellow tinge, but the presence of other oxides prevents this condensation of oxygen, and so the impure tetroxide remains white.

It may now be regarded as settled that the atomic weight of cerium is 140.25, with a small uncertainty in the second decimal place.

J. McC.

Occurrence of Alum as an efflorescence on Bricks. HARRY F. KELLER (*J. Amer. Chem. Soc.*, 1903, 25, 214—215).—Some white brickwork which had been treated with sulphuric acid and then thoroughly washed to remove iron stains, subsequently showed a white efflorescence consisting mainly of potash alum.

A. McK.

Action of Solutions of Bleaching Powder and of Hypochlorous Acid on Metals. ALEX. D. WHITE (*J. Soc. Chem. Ind.*, 1903, 22, 132—134).—Iron, tin, copper, nickel, and cobalt, when immersed in a solution of bleaching powder of sp. gr. 1.040, are rapidly attacked

with the evolution of oxygen. Aluminium and magnesium are similarly attacked, but the gas produced consists almost entirely of hydrogen. Antimony and lead are not acted on, whilst lead and zinc are only slightly attacked.

The effect of sunlight on a solution of bleaching powder is the evolution of a gas consisting of oxygen, 96.3 per cent., and nitrogen, 3.7 per cent.

Hypochlorous acid in aqueous solution slowly attacked strips of iron, tin, copper, nickel, and cobalt, chlorine being liberated in every case. With iron, hydrogen is also formed, and oxygen is found mixed with the chlorine in the copper, nickel, and cobalt experiments. Magnesium is quickly attacked, pure hydrogen being formed, whilst aluminium causes the liberation of both hydrogen and chlorine.

With the exception of tin, aluminium, and magnesium, all these metals cause disintegration of linen fabrics to take place when in contact with the latter in bleaching solutions.

W. P. S.

Spontaneous Decarburisation of Steel. G. BELLOC (*Compt. rend.*, 1903, 136, 500—501).—The author has already proved (*Compt. rend.*, 1900, 131, 336) that when steel is kept at a temperature superior to 800° decarburisation takes place. It has now been shown that this is independent of the atmosphere in which the heating takes place, and even in hydrogen the decarburisation is not diminished. If the steel is placed in a vacuum and then quickly heated, decarburisation takes place.

If the metal is first heated for a long period at about 550°, then at above 800°, no decarburisation takes place. At the lower temperature, the occluded gas is expelled, and the decarburisation is associated with the presence of occluded gas. In the absence of occluded gas, there is a volatilisation of some iron, and the residual carbon combines so as to super-carbonise the steel.

J. McC.

Influence of Certain Treatments on the Micro structure of Nickel Steels. LÉON GUILLET (*Compt. rend.*, 1903, 136, 502—504).—When a nickel steel is tempered without being raised to the temperature of transformation from the non-magnetic to the magnetic condition, no change takes place in its micro-structure. If the nickel steel has a martensite structure, there is a tendency for it to pass into the polyhedral form, but the martensite remains the predominant structure. Only the polyhedral forms of nickel steel are modified by annealing, but whereas the change by tempering only takes place with an alloy, the transformation point of which lies near the ordinary temperature, the change by annealing takes place with a more extended series of alloys. The temperature at which the change takes place by annealing is about 700°. Those nickel steels which are altered by tempering, are likewise changed by cold hammering. When the nickel steel is exposed to a pressure which does not exceed the limits of the elasticity, the cleavage planes become more evident, and when greater pressure is applied the polyhedral form changes. Ordinary nickel steel is not altered in structure when cooled to -78°; at this temperature, the martensite

structure becomes much more marked in a nickel steel already possessing this structure. The irreversible change of non-magnetic into magnetic nickel steel at -78° observed by Dumas (*Annales des Mines*, 1902) does not take place instantaneously. The polyhedral structure is destroyed as the temperature falls, and it disappears completely at -40° .

The change which takes place by cementation and decarburisation has also been studied, but is complicated by the simultaneous annealing which accompanies these processes. J. McC.

Equilibrium which exists between Copper, Silicon, and Manganese, and the Manganese Silicide, MnSi_2 . PAUL LEBEAU (*Compt. rend.*, 1903, 136, 231—233. Compare this vol., ii, 215).—Fused copper silicide containing relatively small quantities of silicon and some second metal such as manganese, cobalt, &c., forms a system in which various quantities of one of the latter metals may react with varying quantities of the silicon; thus, several silicides of the metal may be obtained. Starting with a mixture of 50 grams of copper, 23 grams of manganese tetroxide, Mn_2O_4 , 33 grams of potassium silicofluoride, and 19 grams of sodium, which was heated in a Perrot's furnace, the quantities of the two substances last mentioned have been gradually raised without altering the ratio Cu:Mn. It was found that when the quantity of silicon was less than 10 per cent. the silicide, Mn_2Si (*loc. cit.*), was formed; it remains undissolved on treating the fused mass with nitric acid. On raising the quantity of silicon to 15 per cent., the crystals had the composition MnSi . When a mixture of 14.9 per cent. copper, 80.43 silicon, and 3.25 manganese was used, a third silicide, MnSi_2 , could be isolated; it forms small, dark grey, apparently octahedral crystals having a density 5.24 at 13° ; it is not attacked by nitric or sulphuric acids, but is really soluble in hydrofluoric acid and quickly decomposed by concentrated alkalis.

K. J. P. O.

Molybdic Acid. FRANZ MYLIUS (*Ber.*, 1903, 36, 638—640).—In this communication, the results of the author's study of molybdic acid and the molybdates are summarised. No solid molybdic acid exists corresponding with the telluric acid, H_6TeO_6 . The colourless molybdic acid obtained in aqueous solution corresponds with *allotelluric* acid, with which it agrees in having an infinite solubility in cold water, complex composition, in being soluble in alcohol, in being precipitated in the form of acid salts, and in precipitating solutions of proteids. Of the solid forms of molybdic acid, the yellow acid, H_4MoO_5 , has the greatest solubility in water, and is slowly formed when solutions of molybdates or molybdic acid are treated with nitric or hydrochloric acid. The ordinary solution of ammonium molybdate, containing nitric acid used to estimate phosphates, contains acid ammonium molybdates and molybdic acid, and is unstable, as the acid ammonium salts are liable to crystallise out. An ammonium salt, $\text{NH}_3 \cdot 4\text{MoO}_3 \cdot 6\text{H}_2\text{O}$, has been obtained which loses half its ammonia when heated; it is possibly an octamolybdate, and is formed as small, colourless needles when a given quantity of acid is added to a solution of ordinary ammonium molybdate; from a solution in hot water,

a less hydrated salt separates; it has an acid reaction, precipitates proteids, and does not give a precipitate with nitric acid; in this, it differs from ordinary ammonium molybdate. K. J. P. O.

Molybdic Acid. ARTHUR ROSENHEIM (*Ber.*, 1903, 36, 752—753).—A question of priority (compare Mylius, preceding abstract).

W. A. D.

Uranyl Bromide. WILLIAM ECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1902, 12, 1025—1028).—Uranyl bromide, prepared by the usual methods (*Abstr.*, 1879, 508), is a cream-coloured, deliquescent mass, which evolves bromine on exposure to dry air, and is decomposed into hydrated uranic oxide and hydrogen bromide in moist air; it is soluble in water, forming a yellow solution which, when kept, deposits flocks of the yellow hydrate of uranic oxide; no further decomposition is produced by ebullition of the solution. When heated, uranyl bromide evolves bromine and hydrogen bromide, leaving a residue of uranous oxide. The effects produced by the addition of various reagents to aqueous solutions of uranyl bromide are described in the original. T. A. H.

Polonium. FRITZ GIESEL (*Ber.*, 1903, 36, 728—729).—Radioactive bismuth (polonium) can be purified by Mme. Curie's method (*Phys. Zeit.*, 1903, 234). When the hydroxide is added to an excess of nitric acid, a few yellow, flocculent particles remain undissolved which are phosphorescent and emit only the α - or non-penetrative rays (Marckwald, *Abstr.*, 1902, ii, 508); when the solution is precipitated by the addition of water in successive portions as basic nitrate, the least soluble fractions emit mostly the α -rays, whilst the most soluble fractions ultimately give the β -rays only. If now the partially purified α -material is treated with metallic bismuth according to Marckwald's method, an intensely active product, emitting non-penetrative rays, is obtained.

The α -rays of polonium are best recognised by means of a gelatin zinc sulphide screen, and the β -rays by a screen of barium platino-cyanide; the β -rays of radium affect both screens in the same way.

W. A. D.

Preparation of Colloidal Metal Solutions. FERDINAND HENRICH (*Ber.*, 1903, 36, 609—616).—Colloidal metallic solutions can be prepared by reducing the salts with polyvalent phenols and photographic developers such as "eikonogen." Gold chloride yields, in acid solution, blue, and occasionally green and rose-coloured solutions, but in alkaline solution violet and red solutions which are much more stable; platinum tetrachloride gives brown solutions, silver nitrate a brownish-red solution, and mercurous nitrate a dark brownish-yellow solution. The solutions pass unchanged through a hardened filter and after purification by dialysis, do not deposit metal when boiled. When subjected to an electrical potential difference, the metal passes to the positive pole, leaving a clear liquid round the negative pole. The solutions are not altered by freezing, but are very sensitive to the presence of acids, bases, and salts, especially barium and zinc chlorides. T. M. L.

Pure Rhodium. SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1903, 34, 82—85).—As Palmaer has shown that there is a very close analogy between rhodium and iridium salts, it was thought possible that the chloropentamminerhodium chloride used in the determination of the atomic weight of rhodium might have contained iridium, but a repetition of the determination with a salt quite free from iridium gave the same number as before. The chloropentammine chloride can be freed from iridium completely by transforming it into the xantho-nitrate, and then back into the chloropentamminerhodium chloride; iridium does not appear to form a xantho-salt. The purification may also be effected by heating the salt on the water-bath with nitric acid of sp. gr. 1.40 until no precipitation is obtained when the solution is diluted and treated with silver nitrate; on cooling, rectangular crystals of chloropentamminerhodium nitrate separate. The liquid is added to its own volume of water and the deposited salt filtered and washed, then air-dried, dissolved in warm water, and added to concentrated hydrochloric acid, when iridium-free chloropentammine-rhodium chloride is deposited, from which pure rhodium can be obtained. The salt, however, always contains some nitric acid from which it is freed by treatment first with 7 per cent. sodium hydroxide solution, then with hydrochloric acid.

J. McC.

Mineralogical Chemistry.

Native Arsenic from Montreal. NEVIL NORTON EVANS (*Amer. J. Sci.*, 1903, [iv], 15, 92—93).—A vein in nepheline-syenite at Mount Royal, Montreal, contains native arsenic and calcite, with very small amounts of realgar and pyrites. The arsenic is in large reniform masses with concentric structure; analysis gave:

As.	Sh.	S.	Insol.	Total.	Sp. gr.
98.14	1.65	0.16	0.15	100.10	5.74

L. J. S.

Pebbles of Argentiferous Copper from Mexico. J. J. FITZPATRICK (*Zeit. Kryst. Min.*, 1903, 37, 305; from *Proc. Liverpool Geol. Soc.*, 1900, 8, 451).—Rounded pebbles of native copper with enclosed particles of native silver were found in the river-bed of the Puebla valley near Popocatepetl; two of them weigh 390 and 220 grams respectively. Analysis gave:

Cu.	Sn.	Fe.	Ag.
94.05	2.28	3.57	0.06

L. J. S.

Some Copper Ores: the Zircon Group. S. STEVANOVIĆ (*Zeit. Kryst. Min.*, 1903, 37, 235—256).—*Stylotypite*, *Famatinite*, and *Enargite*.—Specimens of copper ore from the “Caudalosa Costrovirroyna” mine in Peru consist of stylotypite, a luzonite rich in antimony, massive quartz, crystals of enargite, and crystals of tennantite; the several minerals were deposited in the order enumerated. The result of analyses of the massive, black stylotypite are given under I and II, and of crystals under III; sp. gr. 4·77. The mean of these three analyses agrees with the formula $\left(\text{Cu, Ag, } \frac{\text{Zn}}{2}, \frac{\text{Fe}}{2}\right)_3 (\text{Sb, As})\text{S}_3$;

III agrees with this formula after deducting 10·84 per cent. of chalcopryrite, and the material used for the analyses I and II may have been mixed with arsenopyrite. A new analysis of the original stylotypite from Copiapo, Chili, is given under IV; sp. gr. 5·18. Approximate measurements obtained from the rough crystals of stylotypite from Chili and Peru show that the mineral is probably monoclinic [$a:b:c=1\cdot9202:1:1\cdot0355$; $\beta=90^\circ$ about], and isomorphous with xanthoconite and pyrostilpnite. Falkenhaynite appears to be identical with stylotypite:

	S.	Sb.	As.	Bi.	Cu.	Ag.	Fe.	Zn.	Insol.	Total.
I.	23·20	22·15	6·20	1·12	41·50	1·40	2·24	1·54	0·34	99·69
II.	23·20	26·31	4·32	1·12	36·05	1·34	2·76	3·43	1·41	99·94
III.	25·75	16·86	6·28	0·73	43·60	1·44	3·98	0·80	0·41	99·85
IV.	23·12	28·58	—	—	30·87	10·43	6·27	trace	—	99·27
V.	31·01	12·74	9·09	—	45·43	—	0·67	—	0·65	99·59
VI.	32·42	—	19·08	—	48·53	—	—	—	—	100·03

Embedded in the stylotypite from Peru is a massive mineral with a reddish colour and absence of cleavage, sp. gr. 4·47, which gave on analysis the results under V, agreeing with the formula $\text{Cu}_3(\text{As, Sb})\text{S}_4$. This is identical with the mineral from Cerro de Pasco, in Peru, analysed by Frenzel in 1875, and is midway between luzonite and famatinite; for it, the name *antimon-luzonite* or *stibio-luzonite* is proposed.

Crystals and cleavage fragments of enargite from the “Caudalosa Costrovirroyna” mine gave the results under VI, agreeing with the usual formula, Cu_3AsS_4 ; sp. gr. 4·440 and 4·488. A detailed crystallographic description of this enargite is given, and several new forms noted.

Artificial Domeykite.—Measurement of crystals of domeykite (Cu_3As) prepared by G. A. Koenig (*Abstr.*, 1901, ii, 108) proves the substance to be orthorhombic [$a:b:c=0\cdot5771:1:1\cdot0206$]. The crystals are thin, pseudo-hexagonal plates of a steel-grey colour, which quickly becomes brown on exposure to the air; sp. gr. 7·92—8·10. They agree closely in habit with copper-glance, and are isomorphous with dyscrasite (Ag_3Sb).

Zircon group.—Three different kinds of zircon were examined with respect to their sp. gr. and optical properties. (a) Brown pebbles from Ceylon; sp. gr. 4·06, after being strongly heated, 3·965; the refractive indices are slightly changed after heating, but the colour and uniaxiality remain unaltered. (b) Zircons with sp. gr. about 4·7, and optically uniaxial. (c) Green crystal-fragments from Ceylon;

sp. gr. 4.33, and optically biaxial; when heated, this variety becomes optically uniaxial, its colour disappears, and its sp. gr. rises to 4.66, being thus transformed into the second variety.

Crystallographic measurements are given of zircon from several localities, and of artificial crystals of molybdenum dioxide. The topic axes of these are compared with those of members of the cassiterite group.

L. J. S.

Condition of Platinum in the Nickel-copper Ores from Sudbury. CHARLES W. DICKSON (*Amer. J. Sci.*, 1903, [iv], 15, 137—139. Compare Abstr., 1896, ii, 366; 1902, ii, 267).—A sample of chalcopyrite from the Victoria mine, about twenty miles west of Sudbury, Ontario, was dissolved in nitric acid. The insoluble residue consisted of a number of small, brilliant crystals of sperrylite, of which a crystallographic description is given. The platinum in these ores is therefore present as sperrylite (PtAs_2).

L. J. S.

Rickardite, a New Mineral. W. E. FORD (*Amer. J. Sci.*, 1903, [iv], 15, 69—70).—The new mineral occurs as lenticular masses with native tellurium, pyrites, petzite, berthierite, &c., in the Good Hope mine, Vulcan, Colorado. It has a rich purple colour resembling an iridescent tarnish, and the same colour is shown by a fresh fracture and by the fine powder. The mineral is massive and has an irregular fracture: hardness, 3.5; sp. gr. 7.54. The mean of two analyses is: Cu, 40.74; Te, 59.21 = 99.95. This agrees with the formula $\text{Cu}_4\text{Te}_3 = \text{Cu}_2\text{Te}, 2\text{CuTe}$. The mineral is named after T. A. Rickard, of New York, by whom it was found.

L. J. S.

Chemical Studies of Dolomite and Magnesite. ALBERT VESTERBERG (*Zeit. Kryst. Min.*, 1903, 37, 288—290; from *Bull. Geol. Inst. Univ. Upsala*, 1900, [1901], 5, 97—131).—Numerous experiments and determinations were made in respect to the action of cold dilute acetic acid on magnesite, dolomite, dolomitic marl, and limestone, and on calcareous algæ rich in magnesia. The following conclusions, among others, are deduced. Normal dolomite behaves as a true double salt, and not as a mixture of simple carbonates, and the only double salt is $\text{MgCa}(\text{CO}_3)_2$. In none of the specimens examined was there isomorphous mixing of calcite with magnesite or with normal dolomite. Magnesium carbonate occurs in rocks, soils, and calcareous algæ in three forms, namely, as magnesite, dolomite, and a form, probably hydrated, readily soluble in acids.

L. J. S.

Minerals of Victoria. R. H. WALCOTT (*Zeit. Kryst. Min.*, 1903, 37, 310—311; from *Proc. Roy. Soc. Victoria*, 1901, 13, 253—272).—The present list of the minerals and mineral localities of Victoria forms a supplement to J. A. Atkinson's list of 1896. The following analyses, by D. Clark, are given:

Manganocalcite from Buchan: CaO , 49.77; MnO , 4.84; FeO , 1.00; MgO , 0.25; CO_2 , 43.11; insol., 0.82.

Orthoclase from Mt. Taylor: SiO_2 , 62.84; Fe_2O_3 , 1.43; Al_2O_3 ,

20.23; CaO, 0.92; MgO, 10.30; K₂O, 10.09; Na₂O, 3.25; loss on ignition, 1.20.

Zinc-blende from Cassilis: Zn, 63.29; Fe, 4.61; S, 29.88; insol., 0.15.

Wolframite from Buckwong Creek: WO₃, 75.20; MnO, 5.74; FeO, 17.63; insol., 1.24. L. J. S.

Tamanite, a New Iron-calcium Phosphate. S. P. POPOFF (*Zeit. Kryst. Min.*, 1903, 37, 267—268).—In cavities at the junction of a bed of siderite with limonite in the limonite mine "Zelesnyj Rog," on the Taman peninsula (prov. Kuban), there occur, rather abundantly, crusts of green to yellowish-green crystals, the composition of which is as follows:

P ₂ O ₅ .	FeO.	CaO.	H ₂ O.	Total.	Sp. gr.
34.50	20.00	27.72	18.33	100.55	2.812

The corresponding formula is (Ca,Fe)₃(PO₄)₂·4H₂O. Goniometric measurements are given of the triclinic crystals. There are perfect cleavages in two directions. The mineral is closely allied to messelite, but differs from this in containing more water. In an editorial note, added by P. Groth, it is remarked that tamanite is identical with anapaite (*Abstr.*, 1902, ii, 268). L. J. S.

Bowenite from Kashmir. CHARLES ALEXANDER McMAHON (*Zeit. Kryst. Min.*, 1903, 37, 310; from *Mem. Geol. Survey, India*, 1901, 31, 312).—Blocks of sulphur-yellow, greenish-yellow, and apple-green serpentine, which have fallen from Mt. Mango-Gusor (6349 m.), near Shigar, into the valley below, belong to the bowenite variety. Sp. gr., 2.48; hardness, 5; analysis gave:

SiO ₂ .	MgO.	Al ₂ O ₃ .	FeO.	CaO.	H ₂ O.	Total.
41.13	43.65	1.23	1.49	0.17	12.46	100.13

L. J. S.

Conditions of Formation of Orthoclase and Albite. EMIL BAUR (*Zeit. physikal. Chem.*, 1903, 42, 567—576).—Varying quantities of amorphous silicic acid and potassium or sodium aluminate were heated with water in steel tubes for several hours at 520°; after cooling, the contents of the tubes were examined to determine what solid had crystallised out. In this way, it was found that orthoclase and albite are obtained only from solutions containing excess of base. The author's general results, however, cannot well be described without reference to the diagram accompanying the paper. J. C. P.

Melanite from Cortejana, prov. Huelva, Spain. FERNANDO MOLDENHAUER (*Zeit. Kryst. Min.*, 1903, 37, 272).—At the junction between porphyrite and granulite was found brown, moist, clayey masses with crystal-faces, which are pseudomorphs after melanite.

After drying, these brown masses become hard and have the following composition :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	H ₂ O.	Total.	Sp. gr.
34·77	3·30	26·89	0·32	0·71	32·04	0·60	0·45	1·30	100·38	3·7

Rhombic dodecahedra of fresh melanite occur in calcite at the locality.
L. J. S.

[Uvarovite and Hackmanite.] LEON H. BORGSTRÖM (*Zeit. Kryst. Min.*, 1903, **37**, 283—285; from *Geol. För. Förh.*, 1901, **23**, 557—566).—Notes are given of various Finnish minerals; barytes is recorded for the first time from this country.

Uvarovite.—This is found as a thin, crystalline incrustation lining drusy cavities in a quartzite, near the contact of this with serpentinitised olivine-rock, at Sysmä, parish Kuusjärvi, gov. Kuopio. It has a fine emerald-green colour and vitreous lustre; it is isotropic, and the refractive index for green light is 1·8554. When heated, it first becomes cloudy and yellow, and then opaque and black; on cooling, it regains its original clearness and colour. Analysis gave :

SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Total.	Sp. gr.
36·79	1·93	27·54	0·41	32·74	0·50	99·91	3·772

The mineral thus contains 90·2 per cent. of Ca₃Cr₂Si₃O₁₂, and is the purest and freshest calcium-chromium garnet hitherto analysed.

Hackmanite, a new member of the sodalite group.—Together with ægirite and several accessory minerals, hackmanite is a constituent of a new rock called *tawite* from the Tawa valley in the Kola peninsula. It is always developed in idiomorphic, rhombic dodecahedral crystals; it is isotropic, and the refractive index for Na-light is 1·4868. The pale reddish-violet colour of the mineral soon disappears on exposure to daylight. Hardness about 5; sp. gr. 3·32—3·33. Analysis gave :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	Cl.	S.	Total, less O for Cl and S.
36·99	31·77	0·17	0·05	25·84	0·16	6·44	0·39	100·17

The mineral is soluble in hydrochloric acid, when all the sulphur is given off as hydrogen sulphide; the sulphur is thus present as mono-sulphide, and not as polysulphide, NaS₃, as in lazurite. From its composition, hackmanite may be considered to be a sodalite with 6·23 per cent. of the compound Na₄[Al(NaS)]Al₂(SiO₄)₃, a compound which Brögger and Bäckström in 1890 concluded to be a constituent of the artificial product known as "white ultramarine." L. J. S.

Free Phosphorus in the Saline Township Meteorite. OLIVER C. FARRINGTON (*Amer. J. Sci.*, 1903, [IV], **15**, 71—72).—While drilling a hole in this stone, a white "smoke" with pungent, garlic-like odour was observed, and on looking into the drill-hole a luminous spot was seen. Qualitative tests of the powder from the hole showed the pre-

sence of phosphorus. Two other holes were bored, but with no repetition of the phenomena.

L. J. S.

Composition of the Iron of Ovifak, Greenland: Bituminous Coal from Sweden. CLEMENS WINKLER (*Zeit. Kryst. Min.*, 1903, 37, 286—288; from *Öfvers. K. Vet.-Akad. Förh.*, 1901, 58, 495—503).—The terrestrial iron of Ovifak was examined for carbon monoxide, the presence of which as a residuo is suggested by Winkler's theory of the formation of this iron (*Abstr.*, 1900, ii, 598), but none was detected. The following analysis, by P. Iwanoff, is given of a weathered sample of the iron: soluble in water, 2.11 (Fe, 0.57; Na, 0.18; K, 0.11; Mg, 0.01; Cl, 0.68; SO_3 , 0.47; O, 0.01); soluble in *aqua regia*, 89.03 (Fe, 75.34; Ni, 1.85; Co, 0.48; Cu, 0.13; C, 2.29; S, 0.18; Ca, 0.07; Mg, 0.04; Cl, 0.96; SO_3 , 0.06; O, 4.42; H_2O , 3.21); insoluble (silicates), 8.96; total, 100.10. In this weathered material there are, besides normal sulphates and chlorides, the following basic salts of iron: $\text{Fe}_4(\text{OH})_6\text{O}_3$, $\text{Fe}_{14}\text{Cl}_6(\text{OH})_{18}\text{O}_9$, and $\text{Fe}_8(\text{OH})_{22}\text{SO}_4$.

In the alum shales of the Cambrian formation of West Gottland, there occur lenticular masses of a bituminous coal known in Sweden as "Kolm." Analysis of this by H. Liebert gave:

C.	H.	O.	N.	S.	H_2O .	Ash.	Total.
60.24	4.64	3.50	0.50	3.99	4.85	22.28	100.00

The red ash contained:

U_3O_8 .	Fe_2O_3 .	Al_2O_3 .	Mn_2O_3 .	MgO.	CaO.	$\text{K}_2\text{O}, \text{Na}_2\text{O}$.	SO_3 .	SiO_2 .
2.87	19.65	21.14	0.32	1.58	trace	[5.98]	0.60	49.86

Another sample of the ash contained only 1.68 per cent. U_3O_8 .

A. E. NORDENSKIÖLD (*loc. cit.*, 505—513), in remarks on the previous paper, notes that several years ago he detected the presence of variable amounts (1—3 per cent.) of uranium in the ash of the Swedish "Kolm"; there are also small amounts of nickel, zinc, copper, molybdenum, and vanadium, as well as traces of cerite and gadolinite earths. The ash of several other asphaltic and anthracitic minerals from various parts of Sweden, and the ash of the American grahamite, also contain small amounts of uranium. An asphalt which occurs abundantly in the Lilla Kallmora mine contains 13 per cent. of ash, 7 per cent. of which is uranous oxide.

L. J. S.

Physiological Chemistry.

Respiratory Exchange and Temperature in Hibernating Animals. MARCUS S. PEMBREY (*J. Physiol.*, 1903, 29, 195—212).—When the dormouse and hedgehog are active and have a temperature over 30° , the respiratory exchange, although variable, is approximately

equal to that of non-hibernating animals of similar size. When the dormouse is torpid and its temperature about 12° , the exchange is reduced; the discharge of carbon dioxide may be only one-hundredth of what it was before; the absorption of oxygen is not reduced so much; the respiratory quotient may fall to 0.23. In awaking, the temperature may rise 19° in 42 minutes, the exchange increases, and the respiratory quotient rises to 0.75. In the hedgehog, similar results were obtained; the respiratory quotient sinks to 0.51. The low respiratory quotients are explained by the partial combustion of fat and formation of sugar which is stored as glycogen. Corresponding results have previously been described in marmots. W. D. H.

Action of Acids and Acid Salts on Blood Corpuscles and other Cells. S. PESKIND (*Amer. J. Physiol.*, 1903, 8, 404—429. Compare Abstr., 1902, ii, 31).—In continuation of previous work, it is now stated that the precipitating agents do not penetrate far into the corpuscle, but combine with the surface layer. The existence of an envelope to mammalian red blood-corpuscles is regarded as highly probable. The same is true for leucocytes, and probably for all typical cells. The envelope consists of nucleo-proteid, cholesterol, and lecithin. W. D. H.

The Laking of Dried Red Blood-corpuscles. CHARLES CLAUDE GUTHRIE (*Amer. J. Physiol.*, 1903, 8, 441—446).—Experiments are described which show that a number of reagents will lake red corpuscles even after they have been dried. W. D. H.

Glycolysis of Different Sugars. P. PORTIER (*Compt. rend. Soc. Biol.*, 1903, 55, 191—192).—The blood of the dog and rabbit produces glycolysis of dextrose, galactose, lævulose, mannose, and maltose, but not of sucrose, lactose, sorbose, arabinose, and xylose. W. D. H.

Blood Gases during Anæsthesia produced by Amylene. CH. LIVON (*Compt. rend. Soc. Biol.*, 1903, 55, 143—144).—During anæsthesia produced in dogs by amylene, there is no arrest of internal combustion, as with chloroform and ether. On extracting the blood gases, amylene is found as a constituent. W. D. H.

Blood Changes after Hæmorrhage. E. P. BAUMANN (*J. Physiol.*, 1903, 29, 18—38).—Hæmorrhage produces a general deterioration of the blood; the hæmoglobin is more diminished than the red corpuscles; an increase of leucocytes, mainly of the polymorphonuclear kind, occurs; there is an increase of serum-albumin, of fibrin, and of rate of coagulation. If the hæmorrhage occurs during the administration of inorganic iron, the main difference noted from the foregoing is that although the red corpuscles are diminished, the hæmoglobin is raised beyond its original value. If organic iron is given, the change is the same, but not so pronounced. If arsenic is given, hæmorrhage produces the usual changes, except that the leucocytes are diminished.

If both iron and arsenic are given, the deterioration of the blood is less when hæmorrhage occurs than when either drug is given separately. The experiments were made on dogs. W. D. H.

Blood Changes in Epilepsy. ROBERT PUGH (*Brain*, 1902, 25, 501—539).—The alkalinity of the blood falls prior to the onset of a fit in idiopathic epilepsy; when the fit is over, the fall continues; the return to the normal occurs five or six hours later, but the normal in these cases is lower than in perfectly healthy people. The fall after the fit is due to the production of acid substances from the contracting muscles. Leucocytosis, mainly of the small hyaline cells, also occurs, and this is more pronounced in status epilepticus. W. D. H.

The Blood after Administration of Adrenalin. CHARLES H. VOSBURGH and A. N. RICHARDS (*Amer. J. Physiol.*, 1903, 9, 35—51).—Intraperitoneal injection of adrenalin chloride, or its application to the pancreas, causes an increase of sugar in the blood. This reaches its maximum in from one to three hours, and may last for more than fourteen hours. With the hyperglycæmia, the time of extravascular coagulation of the blood is lessened. This also appears to be due to action on the pancreas. The increase of sugar is in great part due to an increased formation of the sugar by the liver. W. D. H.

Bacteriolytic Serum-complements. WARFIELD T. LONGCOPE (*J. Hygiene*, 1903, 3, 28—51).—Human blood-serum contains a number of bacteriolytic complements, and normal persons show slight fluctuations in the amount in their blood. In many prolonged chronic diseases (nephritis, liver-cirrhosis, diabetes), there is a marked decrease, and such persons are therefore very susceptible to infections which prove fatal. Some individuals do not show such reduction, and appear to escape terminal infection in consequence. Hyperleucocytosis is often associated with high complement-content for typhoid and colon bacilli. The serum in some typhoid fever patients shows a diminution in the specific complement for the typhoid bacillus.

W. D. H.

Action of Camphor on the Mammalian Heart and Vessels. HEINRICH WINTERBERG (*Pflüger's Archiv*, 1903, 94, 455—508).—The chief action of camphor on the blood vessels of rabbits, cats, and dogs is to produce dilatation. It has a slight and evanescent action on the vaso-motor centre, which is probably reflex, but the main effect is peripheral. No evidence was found that camphor is favourable to the activity of the heart.

W. D. H.

Biochemical Theories. LEOPOLD SPIEGEL (*Chem. Centr.*, 1903, i, 240—241; from *Fortschr. Med.*, 20, 834—844).—A critical account of recent theories in relation to Ehrlich's hypotheses. The importance of osmotic changes is also insisted on.

W. D. H.

Experiments on the Metabolism of Matter and Energy in the Human Body. WIEBUR O. ATWATER, FRANCIS G. BENEDICT, A. P. BRYANT, A. W. SMITH, and J. F. SNELL (13th *Ann. Rep. Storrs' Agric. Exper. Stat.* for 1900, 96—129).—The results include determinations of nitrogen, carbon, hydrogen, water, and the mineral constituents of the food, excrement, and products of respiration. The potential energy of the food and excrement was determined by means of the bomb calorimeter (compare *Ann. Rep.*, 1894, 135, and 1897, 199), whilst the kinetic energy given off by the subject was measured with the respiration calorimeter.

The results afford a demonstration, which scarcely falls short of being final, of the law of the conservation of energy as applied to the living organism, but the discussion of some of the points is reserved until further data are available. N. H. J. M.

Effect of Muscular Activity on the Digestion and Metabolism of Nitrogen. CHARLES E. WAIT (*Bied. Centr.*, 1903, 32, 116—118; from *U.S. Dept. Agric. Bul.*, 117).—The digestibility of food was not appreciably affected by muscular activity. With regard to the question whether proteids or non-nitrogenous substances are utilised in the exercise of force, it was found that no difference occurred in the amount of nitrogen in the urine which could be attributed to increased nitrogen metabolism due to muscular activity. N. H. J. M.

Salivary Digestion in the Stomach. W. B. CANNON and H. F. DAY (*Proc. Amer. Physiol. Soc.*, 1902, xxviii; *Amer. J. Physiol.*, 8).—Peristalsis at the fundus does not occur in the early stages of gastric digestion, and free acid does not appear until an hour after the arrival of food there. Crackers free from sugar were mixed into a paste with saliva and introduced into the stomachs of cats. These were then allowed to live from 30 to 90 minutes, and the contents of the stomachs removed, and boiled. Sugar was then estimated to Allihn's method; the amount in the cardiac end was from twice to two and a half times as great as in the pyloric end. This ratio is diminished if the food is fluid, if the total amount of food is small, and if the stomach is massaged during life. W. D. H.

Variations in the Acidity of the Gastric Juice in Hysteria. J. SELLIER and JEAN ABADIE (*Compt. rend. Soc. Biol.*, 1903, 55, 107—110).—The variations in the acidity of the gastric juice of a patient during hysterical states were insignificant. W. D. H.

Action of Alcohol on Gastric Secretion. GEORGE B. WALLACE and HOLMES C. JACKSON (*Proc. Amer. Physiol. Soc.*, 1902, xvii—xviii; *Amer. J. Physiol.*, 8).—When alcohol is introduced into the intestine of dogs, it stimulates gastric secretion; this is purely reflex, and does not occur when the gastric nerves are cut. Oil of peppermint acts in the same way. W. D. H.

Digestion of Gelatin. PHOEBUS A. LEVENE and L. B. STOOKEY (*Proc. Amer. Physiol. Soc.*, 1902, xxiii; *Amer. J. Physiol.*, 8).—In the

course of tryptic digestion of gelatin, free ammonia increases as the gelatin is transformed into the primary, and the primary into the secondary gelatoses.

W. D. H.

Proteid Digestion in Man. ERNST HEINRICH (*Chem. Centr.*, 1903, 298—299; from *Münch. Med. Woch.*, 49, 2003—2005).—In healthy persons, experiments with boiled, finely-divided beef show that in the first hour one-third of the proteid is in solution in the stomach. Addition of carbohydrates increases proteolysis by 10 per cent.

W. D. H.

Biological Relation of Proteids and Proteid-assimilation. PHOEBUS A. LEVENE and L. B. STOOKEY (*Proc. Amer. Physiol. Soc.*, 1902, xxiii; *Amer. J. Physiol.*, 8).—The biological individuality of proteids, as shown by the precipitin test, explains the fact that proteid material injected has first to be broken up and then reconstructed into the molecule characteristic of the given animal. Where the breaking down occurs is not yet established, but the opinion is expressed that foreign proteids do not pass the digestive system (liver included) unchanged.

W. D. H.

Intestinal Absorption. RUDOLF HÖBER (*Pflüger's Archiv*, 1903, 94, 337—346. Compare Abstr., 1901, ii, 610).—It is the rule that lipid soluble combinations are absorbed intraepithelially, and those which are insoluble interepithelially. To this rule, iron compounds form an exception; compounds of other heavy metals were investigated, and were all found to obey the rule of interepithelial absorption.

W. D. H.

Influence of the Hydrogen Ion in Peptic Proteolysis. WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, xxxiv; *Amer. J. Physiol.*, 8).—The fact that pepsin shows digestive power only when acid is present implies the dependence of the enzyme on hydrogen ions for its activity. Experiments with various acids support this view. Additional experiments with equi-dissociated solutions are expected to show what influence, if any, the anions have.

W. D. H.

Tyrosinase in Suberites Domuncula. JULES COTTE (*Compt. rend. Soc. Biol.*, 1903, 55, 137—139).—Certain sponges, *Suberites* being mainly examined, contain a tyrosinase in their body juice which turns brown on exposure to air.

W. D. H.

Influence of Exercise on Human Muscle. THOMAS ANDREW STOREY (*Amer. J. Physiol.*, 1903, 9, 52—55).—By means of the ergograph, it was determined that human voluntary muscle is made more irritable by successive excitations. The irritability is greatly increased by a moderate amount of work, but is decreased by a fatiguing amount of work. The "warming up" practice of athletes has, therefore, a rational foundation.

W. D. H.

The Sugars of Muscle. WILLIAM A. OSBORNE and S. ZOBEL (*J. Physiol.*, 1903, 29, 1—8).—The hydrolysis of glycogen by saliva and taka-diastase can proceed as far as dextrose. At 37°, with malt diastase and pancreatic juice, it stops with the formation of maltose. In all cases, an osazone is obtained which melts approximately at 153°. This so-called isomaltosazone is maltosazone, altered by the presence of a dextrinous substance, as Brown and Morris showed in connection with the hydrolysis of starch by malt-diastase. The carbohydrates of muscle, exclusive of glycogen, are dextrans, dextrose, and maltose, the latter sugar preponderating.

W. D. H.

Comparative Study of Sugar in Muscles. CADÉAC and MAIGNON (*Compt. rend.*, 1903, 136, 120—122).—Next to the liver, the heart is the organ which elaborates most sugar; it produces more than other striated muscles; smooth muscle produces but little sugar.

W. D. H.

Action of Drugs on Bronchial Muscles. T. GREGOR BRODIE and W. E. DIXON (*J. Physiol.*, 1903, 29, 97—173).—The vagus nerve, and not the sympathetic, contains both constrictor and dilator fibres for the bronchial muscles. The degree of contraction is best estimated by the plethysmographic method. Ether and chloroform, used as anæsthetics, paralyse the endings of both sets of nerve fibres. Muscarine, pilocarpine, and physostigmine induce bronchiolar constriction. This effect is abolished by atropine. Barium salts, veratrine, bromine, and salts of many heavy metals (for instance, gold) produce constriction which is not influenced by atropine. Inhalation of carbon dioxide leads to constriction which is not altogether central in origin. Chloroform, ether, lobelia, and atropine induce dilatation when constriction is previously present. The effect of lobelia is transient, that of atropine is permanent.

W. D. H.

The Choline Test for Active Degeneration of the Nervous System. F. WALKER MOTT (*Arch. Neurol.*, 1903, 2, 858—862).—The amount of choline in the blood runs parallel with the condition of active degeneration in the nervous system. The amount can be ascertained by the precipitation of the platinichloride from an alcoholic extract of 1—10 c.c. of blood. Notes of the cases are given. The test is of no use to distinguish between organic and functional disease, unless the organic disease is active at the time the blood is drawn. It is therefore specially applicable after the onset of symptoms indicating irritative or destructive processes.

W. D. H.

Presence of Arsenic in the Animal Series. GABRIEL BERTRAND (*Ann. Inst. Pasteur*, 1903, 17, 1—10. Compare *ibid.*, 1902, 16, 553).—A considerable number of animals, ranging from sheep to sponges, were examined, and in every case arsenic was found to be present.

Arsenic is not confined to certain organs, but occurs in all tissues (compare Abstr., 1902, ii, 517 and 694; and this vol., ii, 91 and 92).

N. H. J. M.

Fluorine in Bone and Teeth. JODLBAUER (*Zeit. Biol.*, 1902, 44, 259—267. Compare Abstr., 1902, ii, 34).—There is no essential difference in the amount of fluorine in the bones in herbivora and carnivora; the amount, however, varies greatly in the same animal (0.05 to 0.32). The flat bones have less than the long bones, but the amount in the latter varies also. Teeth, especially the front ones, contain more fluorine than bone. W. D. H.

Iodine in Cells. J. JUSTUS (*Chem. Centr.*, 1903, i, 405; from *Virchow's Archiv*, 1903, 170, 501—517).—By a microchemical method, sections of various animal and vegetable tissues show that iodine is a widely distributed element. In animal tissues, it is found in the thyroid, lymph glands, thymus, kidney, spleen, testis, and suprarenal body. It is mostly present in the nucleus of the cells. W. D. H.

Manganese and Iron in Sponges. JULES COTTE (*Compt. rend. Soc. Biol.*, 1903, 55, 139—141).—Manganese is present in various sponges, especially in the gemmules. Iron also occurs. W. D. H.

Occurrence of Uracil in the Animal System. ALBRECHT KOSSEL and H. STEUDEL (*Zeit. physiol. Chem.*, 1903, 37, 245—247. Compare Ascoli, Abstr., 1901, i, 108; Kossel and Neumann, Abstr., 1899, i, 631).—When thymus nucleic acid is hydrolysed with 10 per cent. (by vol.) sulphuric acid at 150°, it yields a small amount of uracil. The same compound may also be obtained from the testicles of herrings. It has not been proved whether the uracil is a primary decomposition product of the nucleic acid or whether it may not be obtained indirectly from cytosin. J. J. S.

Lecithin in Suprarenal Bodies. LÉON BERNARD, BIGART, and HENRI LABBÉ (*Compt. rend. Soc. Biol.*, 55, 120—122).—The large amount of lecithin in the suprarenal body in different animals justifies the conclusion that these organs secrete or make lecithin. W. D. H.

Lecithin in the Suprarenal Body of the Guinea-pig. PAUL MULON (*Compt. rend. Soc. Biol.*, 1903, 55, 82—83).—The opinion is expressed that lecithin is a variable, but important, constituent of certain fatty particles seen in the guinea-pig's suprarenal body. W. D. H.

Coagulation Temperature of Cell-globulin. F. WALKER MOTT and WILLIAM D. HALLIBURTON (*Arch. Neurol.*, 1903, 2, 727—734).—The physico-chemical cause of death from hyperpyrexia is coagulation of cell-globulin. When this constituent of protoplasm is coagulated, the protoplasm as such is destroyed. The temperature at which such coagulation is produced most easily is 47°, but temperatures as low as 42°, if prolonged, will have the same effect. The changes are readily demonstrable in nervous tissues, and by means of methylene-blue, chromatolytic changes are demonstrable in nerve cells; but as cell-

globulin is widely distributed, there is no doubt that other protoplasmic structures are similarly effected. W. D. H.

Proteids in the Body Fluids. JULIUS JOACHIM (*Pflüger's Archiv*, 1903, 93, 558—604).—The difference now shown to exist between pseudo-globulin and euglobulin renders an examination of the proteids in blood, exudations, urine, &c., necessary. A large number of analyses are given. In pleural fluid, the amount of all three proteid fractions (the two globulins and albumin) is very constant; the amount of euglobulin is increased in pleuritis. In peritoneal fluid, there is a high percentage of globulin (especially of pseudo-globulin) in cirrhosis, and a low percentage (especially of euglobulin) in cases of cancer. In ascites, due to tubercle, there are great variations. In blood serum of men and animals, the tables given show great variations also. The relation of the proteid fractions to toxins and antitoxins is discussed. In nephritic urine, the amount of albumin is greater than that of globulin; euglobulin, however, is absent or present only in traces. In amyloid disease, the amount of globulin of both kinds increases. W. D. H.

Proteids in Exudations. MORITZ (*Chem. Centr.*, 1903, i, 239—240; from *Münch. Med. Woch.*, 49, 1748—1749).—Exudations contain a proteid which is readily precipitable by acetic acid; this has been variously described as a nucleo-proteid, a mucoid, and a globulin. In the present work, globulin characters are ascribed to it; it may occur in urine. It does not occur in transudations. The precipitate is soluble in dilute mineral acids and in excess of acetic acid. W. D. H.

Milk Coagulation. A. S. LOEVENHART (*Proc. Amer. Physiol. Soc.*, 1902, xxxv; *Amer. J. Physiol.*, 8).—The interval between the time the "metacasein reaction" can be obtained and coagulation, varies inversely with the amount of rennin. Soluble calcium salts are necessary for the metacasein reaction. If at the metacasein stage the rennin is destroyed by heating, the addition of calcium chloride at 40° produces a coagulum. This shows that at this stage the caseinogen has been largely transformed into paracasein. Fresh milk can neither precipitate paracasein solutions nor prevent the precipitation of paracasein by calcium chloride. It appears that the calcium salts in milk are altered in some way by rennin, and thus become capable of precipitating paracasein. The calcium salts are probably loosely combined with some constituent of the milk, and these compounds are dissociated by the rennin. W. D. H.

Existence in certain Milks of a Ferment which Decomposes Salol. A. DESMOULIÈRES (*J. Pharm. Chim.*, 1903, [vii], 17, 232—239).—The decomposition of salol into salicylic acid and phenol by human milk and the milk of asses is considered by the author to be a saponification process, and not to be due to a ferment. These two milks are more alkaline than the milk of other animals, and experimental work is described which shows that acidification prevents

the action, and further, that it will proceed in artificially prepared solutions of the requisite and simultaneous acidity and alkalinity.

W. P. S.

Active Components of the Secretions of the Skin Glands of the Toad. EDWIN S. FAUST (*Chem. Centr.*, 1903, i, 347; from *Arch. exp. Path. Pharm.*, 49, 1—6. Compare Abstr., 1902, i, 446).—A reply to Phisalix and Bertrand's criticisms (Abstr., 1902, ii, 576). The presence of bufotenin in the skin of the toad is by no means proved.

E. W. W.

Purine Excretion in Man. RICHARD BURIAN and HEINRICH SCHUR (*Pflüger's Archiv*, 1903, 94, 273—336. Compare Abstr., 1902, ii, 530).—Further experiments in support of the authors' previous conclusions, and criticism of Loewi's results.

W. D. H.

Exercise and Urinary Secretion. G. C. GARRATT (*J. Physiol.*, 1903, 29, 9—14).—Early excretion of sulphuric acid is a constant feature in the metabolism which accompanies rapid muscular exercise (bicycling). It passes out combined with potassium and ammonium, and the maximum output occurs several hours before that of total nitrogen. The increased excretion of phosphoric acid due to exercise bears close relation to that of free acid and urea. The acid is eliminated chiefly in combination with alkali earths and ammonium. The normal relation between sodium and chlorine is not disturbed by exercise, nor is the usual influence of increase of the urinary water on them prevented thereby.

W. D. H.

Comparative Pharmacological Experiments on the Action of Poisons on Unicellular Organisms. W. KORENTSCHEWSKY (*Chem. Centr.*, 1903, i, 347; from *Arch. exp. Path. Pharm.*, 1902, 49, 7—31).—The original paper contains a description of experiments on the action of alkalis, acids, salicylic and benzoic acids and their sodium salts, caffeine, *Caffeinum natrio-salicylicum*, *Caffeinum natrio-benzoicum*, sodium chloride, potassium chloride, potassium iodide, sodium iodide, potassium bromide, sodium bromide, ammonium bromide, veratrine hydrochloride, physostigmine salicylate, strophanthine, strychnine nitrate, atropine sulphate, cocaine hydrochloride, morphine hydrochloride, antipyrine, mercuric chloride, and neutral-red on *Paramecium caudatum* and *Vorticella microstoma*. In many cases, the poisons acted on the infusoria in much the same way as on vertebrates.

E. W. W.

Experiments on the Carbohydrate Acids. PAUL MEYER (*Chem. Centr.*, 1903, i, 474—475; from *Zeit. klin. Med.*, 47, Nos. 1, 2).—The results of experiments on the carbohydrate acids show that dextrose may be directly oxidised to glycuronic acid in the organism, whilst chloralose forms several laxorotatory substances, but only an extremely small quantity of urochloralic acid. Glycuronic acid promotes the separation of oxalic acid and its accumulation in the liver. Gluconic acid is attacked, but not completely oxidised, saccharic acid being excreted in the urine. It is evident, therefore, that whilst the

$\text{CH}_2\cdot\text{OH}$ group may be oxidised in the organism, the CO_2H group is not affected, and this fact is in accordance with the assumption that dextrose may be directly oxidised to glycuronic acid. Saccharic acid is converted into oxalic acid.

From these results, it appears that in some cases an increase in the quantity of glycuronic acid which is excreted may indicate incomplete oxidation of dextrose.

E. W. W.

Toxicity of Epinephrin (Adrenalin). SAMUEL AMBERG (*Proc. Amer. Physiol. Soc.*, 1902, xxxiii—xxxiv; *Amer. J. Physiol.*, 8).—The pathological changes produced by epinephrin consist of hæmorrhages in heart, lungs, liver, and other organs. There is an injurious effect on the heart as well as on respiration; there is an initial stimulation followed by paralysis of the cardiac vagus. Two mg. given intravenously per kilo. of body weight is fatal in dogs; the fatal dose given subcutaneously is 6 mg., and, injected intraperitoneally, 0.5 to 0.08 mg. per kilo. of body weight.

W. D. H.

Action of Ethyl Alcohol on Protoplasm. FREDERIC S. LEE (*Proc. Amer. Physiol. Soc.*, 1902, xix; *Amer. J. Physiol.*, 8).—The contractions of the bell of the medusa *Gonionema* are markedly increased by small doses of alcohol. This agrees with results on striated muscle; larger doses in both cases have an unfavourable effect.

W. D. H.

Origin of Glycuronic Acid. JOHN A. MANDEL and HOLMES C. JACKSON (*Proc. Amer. Physiol. Soc.*, 1902, xiii—xiv; *Amer. J. Physiol.*, 8).—Camphor was given to fasting dogs, and the camphorglycuronic acid estimated in the urine. The amount excreted was lessened by feeding with sugar, and increased by feeding with meat. It is therefore probable that proteid, and not sugar (as Mayer considers), is the source of the acid. It was not discoverable in the blood, and perfusion experiments pointed to the kidney itself as the seat of the synthesis of the glycuronates. The kidney shows fatty degeneration in the ascending loops of Henle, but not in the convoluted tubules.

W. D. H.

Physiological Action of Ipoh and Antiarin. C. G. SELIGMANN (*J. Physiol.*, 1903, 29, 39—57).—Ipoh, the arrow poison of the upas tree, owes its properties to the glucoside antiarin. In frogs, it acts on the heart ventricle like a poison of the digitalin group; it also causes paralysis of the central nervous system and passing clonic spasms of the voluntary muscles. In mammals and birds, there are also gastrointestinal symptoms; some birds are comparatively immune. In some respects, the antiarin prepared for the present work was less active than preparations made by previous investigators.

W. D. H.

Nucleic Acid. LAFAYETTE B. MENDEL, FRANK P. UNDERHILL, and BENJAMIN WHITE (*Amer. J. Physiol.*, 1903, 8, 377—403).—Vegetable nucleic acid from the wheat embryo resembles the guanylic acid of the pancreas in its physiological effects. It produces a fall of arterial

pressure, a lessening of blood coagulability, an increased lymph flow, and a degree of immunity against subsequent injections.

Its ingestion in man is followed by an increased output of uric acid, and in the dog by the excretion of allantoin. These products correspond with only a portion of the purine radicle introduced. In animals, allantoin excretion was observed after the introduction of vegetable nucleic acids into the body per rectum, intravenously, intraperitoneally, and subcutaneously. Some features of intermediary purine-metabolism are discussed.

W. D. H.

Oxaluria. A. M. LUZZATO (*Zeit. physiol. Chem.*, 1903, 37, 225—244).—In the urine of dogs, rabbits, and, to a smaller extent, men, a substance is usually present which, on boiling with hydrochloric acid, yields oxalic acid; this substance is probably oxaluric acid. The addition of ammonium oxalurate to human urine does not produce a sediment of calcium oxalate; the presence of oxaluric acid will not therefore account for a deposit of calcium oxalate. In some unknown conditions, less oxalic acid is obtained in the urine after it has been boiled with hydrochloric acid than before; this is of importance in view of the estimation of this substance. In the animal body, oxaluric acid is converted into oxalic acid and completely oxidised. Administration of uric acid in dogs and rabbits causes no noteworthy increase of oxalic acid excretion; if oxalic acid is formed from uric acid, it appears to be completely oxidised.

W. D. H.

Physiological Action of Proteoses. LAFAYETTE B. MENDEL and FRANK P. UNDERHILL (*Proc. Amer. Physiol. Soc.*, 1902, xvi—xvii; *Amer. J. Physiol.*, 8).—Pick and Spiro consider that the property of retarding blood-clotting is attributable not to pure proteoses, but to an active impurity (peptozyme). In the present research, various proteoses were prepared pure from different proteids, but were found to produce characteristic symptoms, lessened blood-coagulability, fall of arterial pressure, excitation followed by narcosis, lymphagogenic effects, and a degree of immunity.

W. D. H.

Tribromo-ter.-butyl Alcohol. E. M. HOUGHTON and T. B. ALDRICH (*Proc. Amer. Physiol. Soc.*, 1902, xviii—xix; *Amer. J. Physiol.*, 8).—Willgerodt prepared a trichloro-ter.-butyl alcohol, and mentioned that he had made a similar bromo-compound. The present paper considers the pharmacological properties of the latter compound. Although it has decided anaesthetic properties in animals, it has only little influence on the heart or circulation, and recovery occurs without untoward results.

W. D. H.

Albumoses and Peptone Precipitins. ROSTOSKI and SACCONAGHI (*Chem. Centr.*, 1903, i, 529; from *Deutsch. med. Woch.*, 1903, 29, No. 5).—By injection of the proteolytic products of serum-albumin from the horse, obtained by peptic and tryptic digestion, precipitins were obtained which react with albumin and its products; the weakest reaction is with peptone. The precipitins are not destroyed by heat

The paper contains criticisms of previous work, and theoretical deductions on the subject of the constitution of immune substances.

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Antipepsin. HANS SACHS (*Chem. Centr.*, 1903, i, 244; from *Fortschr. Med.*, 20, 425—428).—Animals can be immunised with pepsin and an antipepsin obtained; this emphasises the analogy between ferments and toxins.

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Antilaccase. C. GESSARD (*Compt. rend. Soc. Biol.*, 1903, 55, 227—228).—By the subcutaneous injection of laccase into rabbits, their serum in time develops an antilaccase.

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[Action of Secretin.] ENRIQUEZ and HALLION (*Compt. rend. Soc. Biol.*, 1903, 55, 233—234).—Experiments are described which are mainly confirmatory of the work of Bayliss and Starling. Intra-duodenal injection also produces a flow of bile. There is also a slight fall of blood pressure. The intravenous injection of sodium carbonate favours both biliary and pancreatic secretion.

W. D. H.

Pancreatic Secretion. W. M. BAYLISS and ERNEST H. STARLING (*J. Physiol.*, 1903, 29, 174—180).—Pancreatic secretin is a simple substance of definite chemical constitution, common to all types of vertebrate animals, and not specific for each type. The direct action of secretin is limited to the pancreas; the increase of bile which follows its injection may be indirect. Salivation does not occur if the nerves to the salivary glands have been cut, and is probably due to anæmia of the medullary centres, produced by the depressor substance which usually accompanies secretin. Secretin can only be obtained by extracting the upper part of the small intestine with acid, and from no other part of the body.

W. D. H.

Factors in Bacteriolytic Action. E. W. AINLEY WALKER (*J. Hygiene*, 1903, 3, 52—67).—The amount of complement in a serum varies from hour to hour after the blood is shed. If the serum is left in contact with the clot, the complement steadily increases for a few hours, and then shows progressive diminution. Whipped blood and serum removed from the clot undergo a steady diminution from the first. Complement is a result of disintegration of leucocytes. The administration of excess of immune serum may be as harmful in the course of an infection as its entire omission; in fact, it might bring about a fatal issue by absorbing all the complement and thus arresting normal protective processes.

W. D. H.

Influence of Camphor upon the Excretion of Dextrose in Phloridzin Diabetes. HOLMES C. JACKSON (*Proc. Amer. Physiol. Soc.*, 1902, xxxii—xxxiii; *Amer. J. Physiol.*, 8).—In animals suffering from pancreatic or phloridzin diabetes, the dextrose:nitrogen ratio is 2·8:1, except in the dog, in which animal, during phloridzin diabetes, it is 3·75:1; but if the dog is given camphor, the ratio sinks to 2·8:1. Fatty degeneration, limited to the ascending loops of Henle,

was found. The evidence appears to point to a double origin of the sugar which appears in the urine as the result of the administration of phloridzin. W. D. H.

Flesh Feeding and Gout. MARTIN KOCHMANN (*Pflüger's Archiv*, 1903, 94, 593—621).—Dogs fed on meat only exhibit subacute nephritis, cloudy swelling of the liver, and deposition of pigment in the spleen. The harmful effect, which is produced not only by horse-flesh but also by beef and other kinds of meat, is attributed to increased formation of uric acid. The bearing of such observations on gout is pointed out. W. D. H.

Proteid-free Diphtheria Antitoxin. PRÖSCHER (*Chem. Centr.*, 1903, i, 244—245; from *Münch. med. Woch.*, 49, No. 28).—Diphtheria antitoxin can be obtained which gives no proteid reactions. The antitoxins are believed to be a new class of substances which, although they do not dialyse, are simpler than proteids. W. D. H.

Abnormal Constituents of the Urine in Epileptic Fits. K. INOUE and T. SAIKI (*Zeit. physiol. Chem.*, 1903, 37, 203—218).—In epileptic fits, the temporary albuminuria generally seen is doubtless caused by the interference with oxidative processes and the consequent injury to the kidney cells. The liver functions are also affected, and this accounts for the appearance of paralactic acid in the urine, to which this paper devotes special attention. W. D. H.

Harmfulness of Boric Acid. FRANZ HOFMANN (*Chem. Centr.*, 1903, i, 242; from *Deutsch. med. Woch.*, 28, 832—833).—Boric acid is not innocuous; it is a powerful cell-poison, and, in the quantities in which it is commonly used as a preservative, is harmful. W. D. H.

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vessels by acting on the vaso-motor nerves. The other, called *thalassin*, is soluble in a mixture of alcohol and ether, and produces an urticarial eruption. Both are powerful.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Ozone on the Diphtheria Bacillus and its Toxin. FERNAND ARLOING and MARC TROUDE (*Compt. rend. Soc. Biol.*, 1903, 55, 236—237).—The action of ozone is injurious both to the bacillus and toxin of diphtheria; the colour of the bacillus deepens.

W. D. H.

Decomposition of Salicylic Acid by Mould. FRANK E. LOTT (*J. Soc. Chem. Ind.*, 1903, 22, 198).—In June last, a number of mould colonies were found to have grown in a solution of salicylic acid made in 1892. The solution originally contained 0.08663 gram of salicylic acid per litre, but on testing, the salicylic acid had completely disappeared, no coloration being obtained with ferric chloride. Further experiments with the mould showed that, when allowed to grow in a solution of the above-mentioned strength, the salicylic acid was entirely destroyed in about 5 weeks, the action being more rapid when a little ferric chloride was added.

W. P. S.

Enzymes in Mould Fermentations. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1903, 36, 634—638).—Since it was shown that the alcoholic fermentation brought about by yeast is due to the presence of an enzyme, it has been suggested that the formation of lactic acid in dead animal muscles is also due to an enzyme. Up to the present, no enzyme has been isolated from any of the various bacteria which are capable of converting sugar into lactic acid, or from the bacteria which bring about the oxidation of alcohol into acetic acid. From *Bacillus Delbrücki*, which is probably identical with Lafar's *B. acidificans longissimus*, an enzyme has been obtained by the following process: a pure culture of the bacillus was grown on sterilised tubers at 40—45° and then transferred to sterilised water, from which it was separated by centrifugalising; in order to kill the bacteria, the solid residue thus obtained was treated with acetone and ether (compare Abstr., 1902, ii, 521); the yellowish-brown powder was rubbed up with sand free from calcium carbonate and then placed in a solution of sucrose to which toluene had been added as an antiseptic; the mixture, which was completely sterile, was kept for five days at 42°; little formation of lactic acid took place unless the acid was removed by calcium carbonate, but under these conditions, sufficient lactic acid was obtained to prepare and analyse the zinc salt; it was not ascertained whether the inactive or one of the active modifications was formed.

From the beer-vinegar bacteria, a culture was isolated by growing the bacteria on tubers in the presence of four per cent. alcohol and one per cent. acetic acid, a medium in which other organisms are not able to grow. From this culture, an enzyme was obtained by the method just described which, in the presence of calcium carbonate, rapidly oxidised alcohol to acetic acid.

K. J. P. O.

Development of Yeast in Sugar Solutions without Fermentation. D. IWANOWSKI (*Centr. Bakt. Par. II.*, 1903, 10, 151—154).—A reply to Richter (*Abstr.*, 1902, ii, 681). In highly nitrogenous solutions, yeast loses to a great extent its character as a ferment, whilst its growth is considerably increased. The development of the yeast, at the expense of peptone and fermentation products, after the sugar had been consumed, is relatively slow. In peptone alone, growth only takes place with difficulty.

N. H. J. M.

Alcoholic Fermentation with Yeast Extract (Buchner's Zymase) in Presence of Blood-serum. ARTHUR HARDEN (*Ber.*, 1903, 36, 715—716).—The addition of blood-serum very greatly reduces the rate at which the nitrogen of yeast-extract becomes soluble; the inhibiting effect is almost complete in the case of horse-serum, but is very marked also in the case of the serum from the pig and the dog; egg-albumin, on the other hand, produces no inhibiting effect, but itself undergoes proteolysis. The fact that yeast-extract can only ferment a limited amount of sugar is usually explained by assuming the presence in the extract of a proteolytic enzyme, which soon destroys the agent active in fermentation. In accordance with this view, it is found that the addition of blood-serum to a mixture of yeast-extract and sugar causes an increase of 60—80 per cent. in the amount of sugar fermented—a result most readily explained by the inhibiting effect of the serum on proteolysis of the extract.

T. M. L.

Influence of "Decantation" on the Composition and Bacterial State of Mineral Waters. EDMOND BONJEAN (*Bull. Soc. chim.*, 1903, 29, [iii], 137—142).—Analyses were made of the original water, the deposit on the bottoms of "decanting" reservoirs, the surface "crust," and of the water after "decantation" in the case of the ferruginous waters produced by the Saint-Yorre, Rapaggio, and Appollinaris springs. The results, as tabulated in the original, show that the deposit is principally ferric carbonate or oxide with smaller quantities of calcium carbonate and organic matter, whilst the surface "crust" is chiefly calcium carbonate. Although the presence of the surface "crust" favours the existence of anaërobic bacteria, as shown by the presence of nitrites in the water, mineral waters of this type are not good culture media, and consequently bacteria multiply slowly during the process of "decantation." The species observed were *Aspergillus niger*, *A. albus*, *Bacterium termo*, *Bacillus stolonatus*, *B. roseus liquefaciens*, *B. aureus*, *B. arborescens*, *Micrococcus sulphureus*, *M. luteus*, and *M. cremoides*. The author points out that

"decantation," resulting as it does in a change in the composition of mineral waters, is objectionable from a medical point of view.

T. A. H.

Antibacterial Properties of Peru Balsam. M. PIORKOWSKI (*Chem. Centr.*, 1903, i, 414—415; from *Ber. Deutsch. pharm. Ges.*, 12, 386—391).—The presence of 20 per cent., and even more, of Peru balsam has been found to only very slightly affect the growth of bacteria. A culture of *Pyocyanus*, which had remained in the balsam for 24 hours, when transferred to nutritive medium showed signs of germination. Similarly, 1.5 per cent. of cinnamein and 4 of styracin were not sufficient to effect complete sterilisation. The presence of 2 per cent. of cinnamic acid, on the other hand, was found to impede growth, and 4 per cent. to cause death. Hence it is scarcely possible for Peru balsam to have an antibacterial action.

E. W. W.

Isolation of the Enzyme which effects Anaërobie Respiration in the Cells of the Higher Plants and Animals. JULIUS STOKLASA and F. CZERNY (*Ber.*, 1903, 36, 622—634).—It has been demonstrated that anaërobie respiration, which occurs in the tubers of sugar beet and potatoes and in peas, causes a conversion of the carbohydrates into alcohol and carbon dioxide, that is, an alcoholic fermentation; the change is brought about by an enzyme which is contained in, or formed by, the cells.

The tubers of sugar beet or potatoes, from which the ferment was isolated, were sterilised and allowed to respire anaërobieally for several days; within a short time, vigorous alcoholic fermentation had begun. The tubers, &c., were then rubbed up to a thin paste and the sap pressed out at a pressure of 300 atmospheres and filtered through linen. The proteid was precipitated by means of alcohol and ether, and from the liquid thus obtained the ferment thrown out by further treatment with alcohol and ether. This precipitate, which is but small, was dried at 20—30° and retains its activity for 5—7 days.

The experiments with the ferment were carried out in such a manner that the carbon dioxide and the alcohol could both be estimated; they were found to be in mol. proportion. Great precautions were taken to ensure that the mixtures were sterile. In most cases, potassium metarsenite or thymol were added. Further, when bacteria were known to be present, it was always shown that they were not able to convert the carbohydrates, at least under the conditions, into alcohol and carbon dioxide.

The enzyme obtained from the sugar beet (*Beta vulgaris*) was found to be exceedingly active; it attacked dextrose more rapidly than lævulose. Similar results were obtained with the potato (*Solanum tuberosum*) and with the pea (*Pisum sativum*).

It was also demonstrated that both in the pea and the beetroot, it is not necessary to let the peas or the tuber respire anaërobieally; the glycolytic enzyme was present in, and could be isolated from, the fresh plant.

The fermentation in all the experiments began at once, and was most active after 24 hours; it had completely ceased after 62 hours.

An enzyme of similar properties has been isolated from the leaves and fruit of plants, the ferment obtained from the former being exceptionally active.

From various animal organs, the lungs, heart, liver, and muscles of cattle, a ferment has been isolated, which has very active glycolytic properties; a temperature of 37° , the normal mammalian temperature, is the optimum temperature for this enzyme. K. J. P. O.

Vegetation in Atmospheres Rich in Carbon Dioxide. EM DEMOUSSY (*Compt. rend.*, 1903, 136, 325—328).—Lettuce, tobacco, and colza were grown in sand with ordinary air and with air containing an excess of carbon dioxide. Greatly increased growth was obtained when the carbon dioxide was obtained from soil or from liquid carbon dioxide slowly diffused through water under the ordinary pressure. Whilst the plants grown in air alone weighed less than 1 gram, the weight was increased to 17.5 and 33 grams when the amount of carbon dioxide was raised to 15 and 25 respectively in 10,000.

When, however, the carbon dioxide was prepared from marble and hydrochloric acid, the plants soon became yellow, even when the gas was passed through several flannel filters and columns of solid potassium carbonate, and the amount reduced to 7 in 10,000.

The unfavourable results obtained by Brown and Escombe (*Abstr.*, 1902, ii, 682) are attributed to impurities in the carbon dioxide (compare Dehérain and Maquenne, *Abstr.*, 1882, 639). N. H. J. M.

Breaking down of Tyrosine in Seedlings. R. BERTEL (*Chem. Centr.*, 1903, i, 178; from *Ber. deut. bot. Ges.*, 20, 454—463).—Tyrosine is produced abundantly in seedlings of *Lupinus albus* from the reserve proteids of the cotyledons, and is partially oxidised by an enzyme in the upper parts of the roots, yielding a substance identified as Wolkow and Baumann's homogentisic acid. This substance, which reduces silver nitrate, is further oxidised in the lowest portions of the roots; the product has no reducing action on silver nitrate.

There is also a migration of tyrosine to all the growing portions of the plant, where it takes part in the production of proteids.

N. H. J. M.

Proteolytic Enzymes in Plants. SYDNEY H. VINES (*Ann. Bot.*, 1903, 17, 237—264).—The results of numerous experiments with different parts of Phanerogams (fruits, bulbs, tubers, stems, leaves, roots, and seeds), the leaves of a fern, and with a mushroom showed, in nearly every case, the presence of a proteolytic enzyme which digested "Witte-peptone" (a mixture of albumoses and some peptone). The exceptions were the pulp and juice of apple and orange.

Fibrin was digested by *Cucumis sativa*, *Euphorbia Characias*, wheat-germ, *Cucumis melo*, and *Agaricus campestris* and, when alkaline, by the bulbs of tulip and hyacinth. No action was observed in the case of vegetable marrow, tomato, and orange.

Egg-albumin was digested by mushroom, but not by cucumber, carrot (root), and leaves of *Tropaeolum* and lettuce. Casein was

digested by melon and mushroom, but negative results were obtained with cucumber, orange-peel, and leaves of *Phalaris* and *Tropaeolum*. The caseinogen of milk is, however, more tractable in some cases.

Liquids or tissues which show a distinct reaction with guaiacum, with or without hydrogen peroxide, were found to be proteolytic, whilst absence of the guaiacum reaction is coincident with deficient proteolytic activity. It is suggested that oxydase or peroxydase may be concerned with the formation of the enzyme, and may effect the liberation of the enzyme from its zymogen.

Insectivorous plants differ from other plants only in the fact that they secrete their enzyme instead of retaining it within the tissues. The results are to be considered as applying only to a particular season, August to November.

N. H. J. M.

Rôle of Oxidising Diastases in the Preparation of Tea and their Influence on Sumach Leaves. KEIJIRÔ ASÔ and M. EMM. Pozzi-Escot (*Chem. Centr.*, 1903, i, 243; from *Rev. gén. Chim. pure et appl*, 5, 419—421. Compare Abstr., 1902, ii, 679).—In addition to an oxydase, tea contains a reducing diastase, *jaquemase*, which seems to be identical with catalase.

The red colour which sumach leaves acquire is also coincident with a loss of tannin, probably due to an oxydase. The dye is soluble in ether, and its alcoholic solution becomes blue in presence of guaiacol.

N. H. J. M.

Occurrence of Zinc in Fruit Juices and Wines. G. BENZ (*Zeit. Nahr. Genussm.*, 1903, 6, 115—116).—The author has frequently found considerable quantities of zinc in fruit juices and wines, the contamination being due to the juices having been stored or fermented in zinc or galvanised iron pans. In some cases, the amount of zinc was large enough to be detected by the taste.

W. P. S.

Occurrence of Copper in Grape Juice and Wine. THEODOR OMEIS (*Zeit. Nahr. Genussm.*, 1903, 6, 116—117).—Traces of copper may be detected in grape juice from unsprayed vines, but, provided that the spraying with copper solution is done at the right time, the fermented wine is free from copper, any of the latter present being removed by the yeast. A possible source of contamination of the wine is from the cellar utensils, as these usually consist of copper or its alloys.

W. P. S.

Action of Manganese Compounds on Plants. OSCAR LOEW and S. SAWA (*Bul. Coll. Agric. Imp. Univ. Tokyo*, 1902, 5, 161—172. Compare T. Schroeder, *Forstchem. u. pflanzenphysiol. Unters. Tharand*, 1878; Ramann, *Bot. Centr.*, 1898; Pichard, *Compt. rend.*, 126, 550; Birner and Lucanus, *Landw. Versuchs-Stat.*, 8, 128; Wagner, *ibid.*, 13, 69 and 278; Giglioli, Abstr., 1902, ii, 527; and Asô, *ibid.*, ii, 679).—Water-culture experiments with barley, and soil culture experiments with rice, peas, and cabbage, in which the plants were grown both with and without manganous sulphate, are described. It was found that whilst moderate amounts of manganese injure the plants

by bleaching the chlorophyll, highly dilute solutions are not only without injurious effects, but induce an increased development. It is considered probable that very fertile soils are characterised by the presence of readily available manganese.

Plants which were injured by an excess of manganese were found to show more intense oxydase and peroxydase reactions than the control plants.

Manganese had no decided stimulating action on yeast and *Aspergillus* (compare H. Molisch, *Wien. Akad. Ber.*, 1894). N. H. J. M.

Physiological Influence of Manganese Compounds on Plants. KEIJIRŌ Asō (*Bul. Coll. Agric. Imp. Univ. Tokyo*, 1902, 5, 177—185. Compare preceding abstract and Ōno, *Journ. Coll. Science Imp. Univ. Tokyo*, 13, pt. 1).—Water-culture experiments with radishes, barley, wheat, and peas are described. It was found that manganese salts have both an injurious and a stimulating effect, which respectively diminish and increase with dilution. Solutions containing 0.002 per cent. of manganous sulphate stimulated the growth in each case, and the plants containing manganese showed the colour reactions of the oxidising enzymes with greater intensity than the control plants.

The presence of iron seems to counteract the action of manganese to some extent. N. H. J. M.

Chemistry of the Stem of *Derris Uliginosa*. An Eastern Fish Poison. FREDERICK B. POWER (*Pharm. Arch.*, 1903, 6, 1—14).—An investigation of the stem of *Derris uliginosa* has shown that no alkaloid is present. The bark yields 9.3 per cent. of tannic acid, equivalent to 6.3 per cent. in the whole stem. The stem also contains gum, sugar, potassium nitrate, hexoic, arachidic, and stearic acids, ceryl alcohol, two isomerides of cholesterol, and two resins, one of which is soluble in chloroform, the other insoluble. Of the cholesterol, one is present in relatively small amount, melts at 207—209°, and is sparingly soluble in alcohol; the other, which constitutes the larger portion, melts at 190—192°, is freely soluble in alcohol, and in chloroform solution has $[\alpha]_D + 25.5^\circ$. When the resin which is soluble in chloroform is heated with alcoholic hydrogen chloride, a substance is obtained which crystallises in yellow needles, melts at 212—213°, and is sparingly soluble in cold alcohol. On fusion with potassium hydroxide, the resin yields acetic and valeric acids together with a small quantity of a substance which gives a violet coloration with ferric chloride. When the resin is oxidised with nitric acid, a small amount of behenic acid is produced, together with oxalic acid and a pale yellow, crystalline *nitro*-compound, which melts at 170—172°. The insoluble resin forms an amorphous, chocolate-brown powder; when heated with dilute sulphuric acid, it yields dextrose and a substance which crystallises in colourless, micaceous scales and melts at about 230°. By the action of fused potassium hydroxide on this resin, acetic and protocatechuic acids are produced, whilst on oxidation with potassium permanganate, oxalic acid is formed.

The toxic effect of the plant is probably due to some constituent of the resin which is soluble in chloroform. E. G.

Protoplasm and Enzymes. THOMAS BOKORNY (*Pflüger's Archiv*, 1903, 93, 605—640. Compare Abstr., 1902, ii, 128).—The opinion is expressed that the different actions of protoplasm justify the assumption that there are different varieties of protoplasm in cells. Anabolic activity in fungi is not hindered by 1 per cent. of mineral acid; this amount of acid inhibits the activity of most enzymes. Alkali similarly affects enzymes more readily than it does protoplasm. There are agents which affect protoplasm harmfully, and are not harmful to enzymes, and *vice versa*. In this relation, the concentration of the poison and the temperature are factors to be considered. Among enzymes, zymase is nearest to protoplasm in the way in which it is influenced by external agents. W. D. H.

Hydrogen Cyanide in Cigar Smoke. HERMANN THOMS (*Zeit. physiol. Chem.*, 1903, 37, 250. Compare Habermann, this vol., ii, 174).—Attention is drawn to the fact that the author has already proved the presence of hydrogen cyanide in tobacco smoke (Abstr., 1900, ii, 428) and has even estimated the amount. J. J. S.

Action of Sulphur Dioxide on Plants. A. WIELER (*Chem. Centr.*, 1903, i, 346—347; from *Ber. deut. bot. Ges.*, 20, 656—666. Compare *ibid.*, 18, 348).—The chloroplasts are probably affected by sulphur dioxide in such a manner as to prevent the regeneration of chlorophyll, and as the latter diminishes there is a falling off of starch production. There is no diminution in the amount of water taken up, as stated by von Schroeder, provided that the leaves remain uninjured. N. H. J. M.

Fixation of Atmospheric Nitrogen by Alfalfa on Ordinary Prairie Soil under Various Treatments. CYRIL G. HOPKINS (*J. Amer. Chem. Soc.*, 1902, 24, 1155—1170).—Pot experiments are first described in which lucerne was grown in black prairie soil, both with and without inoculation, and with various manures. The yield was considerably increased by inoculation (with an extract of a lucerne soil), even when nitrogen was applied as manure. Phosphatic or potassium manures had no effect without inoculation, but were effective when the plants were inoculated or when nitrogenous manure was applied.

Field experiments were made on similar soil, some plots being inoculated with lucerne soil. Inoculation about doubled the yield of both when no manure was applied, and when lime or lime and phosphoric acid were applied. The yield was considerably increased by lime and phosphoric acid, and somewhat increased by lime alone.

From the results of the pot experiments, it is calculated that when inoculated the lucerne accumulated 46.42 lb. of atmospheric nitrogen per acre, the amount obtained from the soil in the pots which were not inoculated being 3.77—7.31 lb. per acre. The percentage of

nitrogen in the dry matter was raised, by inoculation, from 2.59 to 3.62. Similar results were obtained in the field experiments.

N. H. J. M.

Fixation of Phosphoric Acid in the Soil. J. T. CRAWLEY (*J. Amer. Chem. Soc.*, 1902, 24, 1114—1119).—Double superphosphate (10 grams) was applied in each case to the soil contained in boxes (9 × 9 × 9 ins.) with perforated bottoms, and 4800 c.c. of water added. The phosphoric acid in the drainage, and the time required for percolation were determined. The depth of the soil varied from 1 to 6 inches. The soils employed were a dark coloured soil from Makiki, and a typical red Honolulu soil.

It was found that nearly the whole of the phosphoric acid remained within six inches of the surface, and that more than half remained in the first inch of the soil.

To ascertain the total capacity of the soil to fix phosphoric acid, 800 grams of the red soil were mixed with 50 grams of double superphosphate ($P_2O_5 = 20.58$ grams), kept damp, and the phosphoric acid soluble in water determined from time to time. After 1, 3, 8, and 22 days, it was found that 41.6, 57.7, 73.0, and 85.65 per cent. respectively of the phosphoric acid had become fixed. The last amount would represent 181 tons of acid phosphate per acre, 1 foot deep.

It was previously shown that Hawaiian soils are much more basic than those of the United States.

N. H. J. M.

Analytical Chemistry.

Estimation of Sulphur and Phosphorus in Plant Substances. C. P. BEISTLE (*J. Amer. Chem. Soc.*, 1902, 24, 1093—1100).—Fusion with potassium hydroxide and potassium nitrate gave the highest results for sulphur in the case of cotton-seed meal, timothy hay, and egg-albumin. Other methods, including ignition in a bomb-calorimeter, combustion in a stream of oxygen, and incineration after previous saturation with solutions of barium hydroxide and calcium acetate, all yielded lower results (compare Abstr., 1902, ii, 425). The fusion method also gave the highest percentages of phosphorus. W. P. S.

Estimation of Sulphur and Phosphorus in Organic Materials. H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1902, 24, 1100—1109).—For the estimation of sulphur, the method of combustion in compressed oxygen is preferred. Equally good results were obtained by fusing the substance with sodium hydroxide, the latter being prepared by heating sodium peroxide with a little water in a silver crucible. The nitric acid method (Abstr., 1902, ii, 425) gave low results. In the estimation of phosphorus, practically identical

results were obtained whether the material was burnt in a current of oxygen, heated with a mixture of sodium carbonate and potassium nitrate, or boiled with sulphuric acid and ammonium nitrate. The substances examined were dried lean beef, dried curd, yolk and white of egg, wheat bran, and beans.

W. P. S.

Rapid Method for Estimating Sulphur in Coal and Coke.

CARL SUNDSTRÖM (*J. Amer. Chem. Soc.*, 1903, 25, 184—186).—*Coke*.—0.7 gram of the finely powdered coke is mixed with 13 grams of dry sodium peroxide and placed in a covered nickel crucible of about 30 c.c. capacity. The crucible is supported on a triangle and placed in about $\frac{3}{4}$ inch of water. The mixture is then ignited by means of a fuse of guncotton previously washed free from acid, soaked in saturated potassium nitrate solution, and dried.

Coal.—A small steel bomb is employed instead of the nickel crucible, as the combustion is accompanied with explosive violence. The cover of the bomb is insulated from the sides by a thin mica gasket, and from the screw-down device by a piece of ordinary red fibre. Ignition is brought about by fusing an iron wire, one end of which is inserted under the mica gasket and touching the bomb, the other end being above the gasket and in contact with the cover. The wire is looped to touch the mixture, and a current of 4 amperes is used to fuse the wire.

In both cases, the fused mass is treated as usual.

W. P. S.

Organically Combined Sulphurous Acid in Foods.

WILHELM KERP (*Zeit. Nahr.-Genussm.*, 1903, 6, 66—68).—Part of the sulphurous acid present in fruit juices and dried fruits preserved with this substance is considered to be in organic combination, for on adding iodine solution to the acidified aqueous extract of the fruit until a blue coloration just appears, starch solution being used as indicator, further quantities of iodine must be added from time to time to render the colour permanent. This gradual liberation of the residue of sulphurous acid is also exhibited by solutions of sugars containing sulphurous acid and also by the compound of acetaldehyde and sodium hydrogen sulphite.

W. P. S.

Estimation of Selenium in Organic Compounds.

ROBERT E. LYONS and F. L. SHINN (*J. Amer. Chem. Soc.*, 1902, 24, 1087—1093).—A weighed quantity of the substance is heated with fuming nitric acid in a sealed tube for one hour, or longer, at a temperature of 240°. The contents of the tube are then transferred to a basin of about 400 c.c. capacity, and evaporated to dryness after adding one-fourth more silver or zinc nitrate than is theoretically required to unite with the selenious acid present. When dry, the sides of the basin are washed down with a little water, and the evaporation repeated. The residue is treated twice with 50 c.c. of dilute aqueous ammonia and evaporated after each addition. After completely removing any free ammonia by twice evaporating with a little water, the residue is extracted with water, collected on a filter, and washed until free from nitrates. The precipitate on the filter is then decomposed with 10 c.c. of hydrochloric acid of sp. gr. 1.124, the solution diluted with

water to 300 c.c., cooled with ice, and a slight excess of $N/10$ sodium thiosulphate solution is added. After 1 hour, the excess of the latter is titrated with standard iodine solution. One c.c. of $N/10$ sodium thiosulphate is equivalent to 0.001975 gram of selenium.

The selenium may be estimated gravimetrically by decomposing the silver precipitate with hydrochloric acid, filtering, and reducing the selenious acid in the filtrate by means of sodium hydrogen sulphite. Should zinc nitrate be used, filtration after the decomposition with hydrochloric acid may be omitted.

W. P. S.

Estimation of Selenium in Organic Compounds. HEINRICH FRERICHS (*Arch. Pharm.*, 1902, 240, 656—658).—About 0.2—0.3 gram of the substance is decomposed as in the Carius method with nitric acid of sp. gr. 1.4 and about 0.5 gram of silver nitrate. The contents of the tube are rinsed into a porcelain basin and evaporated to dryness. The residue is stirred with a few drops of water, rinsed with alcohol on to a filter, and washed with alcohol until hydrochloric acid no longer precipitates silver in the filtrate. The filter, with the residue, is then boiled with 20 c.c. of nitric acid and 80 c.c. of water until the residue has dissolved entirely; about 5 minutes suffice for this. About 100 c.c. of water and 1 c.c. of concentrated ammonium iron alum solution are then added, and the liquid is titrated with $N/10$ potassium thioeyanate solution; 1 c.c. of this corresponds with 0.00395 gram of selenium. In 14 estimations made with different substances, the maximum error was 0.8 of the total quantity of selenium; in most cases, it was less than half this.

Silver selenite and selenate, although slightly soluble in water, are practically insoluble in 90—95 per cent. alcohol. The precipitate obtained in the experiment must be silver selenite, for this substance is not converted appreciably into selenate when heated with concentrated nitric acid, even at 300°. The weight of the precipitate is somewhat greater than corresponds with this assumption; probably it is contaminated with some silver sulphide due to the presence of hydrogen sulphide in the air of the laboratory.

Selenium can be estimated in the presence of halogens by boiling the precipitate with dilute nitric acid, weighing the residue of silver halide, and estimating the selenium in the solution as above.

C. F. B.

Selenium in Coke. JAMES F. SMITH (*J. Soc. Chem. Ind.*, 1903, 22, 201).—The following method was adopted for estimating selenium in coke. From 100 to 200 grams of the coke were treated on the water-bath with hydrochloric acid and potassium chlorate until nothing more could be extracted than was precipitated by hydrogen sulphide. After filtering and washing, the filtrate was heated until all chlorine had been removed, then reduced by the addition of a slight excess of sulphurous acid, and again heated to expel excess of the latter. The solution was then precipitated by saturating it with hydrogen sulphide (compare *Trans.*, 1884, 45, 699) at a temperature of 70°, the precipitate, after the lapse of 16 hours, being collected on a filter, washed, digested with ammonium sulphide, and again filtered.

The sulphides in the filtrate were reprecipitated by means of hydrochloric acid, collected on a small filter, washed, and dried at 100°. The dry sulphides were then treated with a mixture of potassium cyanide and sodium carbonate and reduced by heating in a current of carbon dioxide according to the process of Babo and Fresenius. The first precipitate obtained from the residue was reduced a second time, and the red precipitate from this second reduction purified by dissolving in a saturated solution of potassium cyanide and reprecipitating by means of hydrochloric acid. The final product was dried at 100° and then over sulphuric acid until constant in weight. From mere traces to 0.015 per cent. of selenium was found in coke from various parts of Yorkshire.

W. P. S.

Gravimetric Estimation of Tellurium. R. W. EMERSON McIVOR (*Chem. News*, 1903, 87, 17).—The author has investigated various gravimetric methods of estimating tellurium, and finds that those in which the precipitant is sodium hydrogen sulphite, or hydriodic and sulphurous acids together, or magnesium, are accurate, provided that precautions are taken to prevent the oxidation of the tellurium precipitate.

D. A. L.

Estimation of Nitrogen in Nitrates and Nitric Esters. ALFRED WOHL and OTTO POPPENBERG (*Ber.*, 1903, 36, 676—684).—Instead of measuring the volume of nitric oxide produced by the action of mercury and sulphuric acid on the nitrate, as in Lunge's method, the decomposition with sulphuric acid and mercury is carried out in an exhausted flask, which is thoroughly shaken until the whole of the nitrate has dissolved, and the pressure in the flask is then determined by means of a manometer. The only serious source of error is the possible formation of oximes by the action of nitrous acid on certain constituents of gelatinised powders, and this is best overcome by adding chromic acid to the sulphuric acid. Corrections are needed for the difference from the standard weight of the quantity of substance weighed out, and for the difference of the temperature from 20°; tables are given showing the magnitude of these corrections. Methods are also described of correcting for the volume of air left in the exhausted flask, and of calculating the standard weight of substance that must be taken in order that the increase in mm. of the pressure in the flask may be a simple multiple of the percentage of nitrogen in the compound analysed.

T. M. L.

Estimation of Nitric Acid in Water. GUSTAV FRERICHs (*Arch. Pharm.*, 1903, 241, 47—53).—The method proposed is to convert the nitrates into chlorides and determine the amount of these by titration with silver solution. A preliminary test of the water is made with diphenylamine. If a deep blue coloration is obtained, 100 c.c. of the water is taken; if but a slight coloration, a larger amount in proportion. The water is evaporated to dryness (by weighing the residue, the total solids can be determined in the same experiment), the residue digested with water, the extract filtered into a porcelain dish, mixed with 50 c.c. of 25 per cent. hydrochloric acid, and evaporated to dryness on a water-bath; no pungent acid odour must remain, and

there must be no drops of condensed acid liquid on the upper rim of the dish. About 30—50 c.c. of distilled water are then added, the absence of nitrates is controlled by testing a drop of the solution with diphenylamine, and the bulk of the solution is then titrated with a standard silver solution. Corrections must be applied for the chloride originally present in the water, and for the chloride left when 50 c.c. of the hydrochloric acid used is evaporated; the former is determined in any case in the ordinary course of a water analysis, and the amount of the latter can be determined once for all in a large sample of acid reserved for this determination.

If the amount of chlorine in the water is very large, exceeding, say, 30 parts per 100,000, it is desirable to remove most of it by adding to 300 c.c. of the water, 4 milligrams of dry powdered silver sulphate for every 1 of chlorine present, digesting for a time in a warm place, filtering, and determining the nitrate as above in a portion of the filtrate. Should alkali carbonates be present, a little barium or calcium chloride must be added to the water; the chlorine now present must be determined, and the determination of the nitrate carried out as before.

C. F. B.

Estimation of Ammonia in Sugar Beets and the Products thereof. E. SELLIER (*Chem. Centr.*, 1903, i, 419; from *Rev. gén. Chim. pure appl.*, 1902, 5, 325—332, 347—351).—A criticism of the various methods from time to time proposed. Distillation with magnesium oxide gives untrustworthy results. Schlössing's process (expulsion of ammonia by milk of lime in the cold), Rümpler's phosphotungstic acid method, and the precipitation with platinic chloride are also defective; in fact, up to the present time a method does not exist which is not interfered with by amino-compounds.

L. DE K.

Iodometry of Hydrazine. ERWIN RUPP (*J. pr. Chem.*, 1903, [ii], 67, 140—142).—Stollé's iodometric method of estimating hydrazine (this vol., ii, 100) has been previously described by Spiess (*Inaug. Diss.*, 1902). Hydrazine sulphate is dissolved in aqueous potassium hydrogen carbonate, left for 15 minutes with excess of *N*/10 iodine, and the excess then estimated with thiosulphate. The use of sodium potassium tartrate or sodium acetate in place of potassium hydrogen carbonate to neutralise the hydriodic acid formed, is found to give the best results.

E. F. A.

Colorimetric Estimation of Small Quantities of Phosphoric Acid and Silica. F. P. VEITCH (*J. Amer. Chem. Soc.*, 1903, 25, 169—184).—The following method is intended for the analysis of drainage waters and of aqueous extracts of soils. A preliminary test is made to ascertain whether the water contains much iron, more than 20 parts per million interfering with the results. A measured volume of the water or extract is then freed from suspended matter by filtration or by evaporating to dryness and filtering. Five c.c. of nitric acid of sp. gr. 1.07 and 4 c.c. of molybdate solution are added to the clear water, and after 30 minutes the coloration is compared

with that produced by known amounts of phosphoric acid. Another portion of the water is evaporated twice to dryness, with an intervening filtration, after adding 3 c.c. of nitric acid and a little magnesium nitrate, heated for 2 hours in a water-oven, treated with 5 c.c. of nitric acid, filtered, washed until about 45 c.c. of filtrate are obtained, and the phosphoric acid colorimetrically estimated as above. This result is subtracted from the first after calculating both to the same volume of water, and the difference multiplied by 0.55 gives the silica. The water should not contain as much phosphoric acid as will cause a precipitate of ammonium phosphomolybdate to form.

W. P. S.

Simplification of Phosphate Analyses. MAX PASSON (*Zeit. angew. Chem.*, 1903, 16, 52—54).—The special form of pipette previously recommended (*ibid.*, 1901, 14) for the introduction of the citrate solution in the estimation of phosphates has now been modified; the lumen of the tube above the widened portion of the pipette is made the same as that of the lower portion. Examples of the results with the two forms of the pipette are given.

K. J. P. O.

Estimation of Citrate-soluble Phosphoric Acid. WILHELM NAUMANN (*Chem. Zeit.*, 1903, 27, 120—121).—Five grams of basic slag are shaken with 500 c.c. of 2 per cent. solution of citric acid for half an hour. One hundred c.c. of the filtrate are mixed with 8 c.c. of nitric acid and boiled down to 25 c.c. When cooled a little, a mixture of 25 c.c. of sulphuric and 5 c.c. of nitric acid is added, and the whole heated until white sulphuric fumes are evolved, which usually takes place after 10 minutes. The liquid now free from silica is afterwards diluted with water and when cold further diluted to 250 c.c.; 125 c.c. of the filtrate (0.5 gram sample) are then first mixed with 35 c.c. of ammonia, and when cold a mixture of 50 c.c. of 24 per cent. ammonium citrate solution and 25 c.c. of magnesium mixture is added. The precipitation is complete when the mixture has been shaken for half an hour.

L. DE K.

Iodometry of Hypophosphites and Hypophosphates. ERWIN RUPP and A. FINCK (*Arch. Pharm.*, 1902, 240, 663—675).—Phosphorous acid and normal phosphites only react very slowly with iodine, but the latter do so comparatively rapidly in the presence of an alkali hydrogen carbonate (this vol., ii, 41); hypophosphites, on the contrary, are not appreciably oxidised in alkaline solution, but hypophosphorous acid is oxidised, and the more rapidly the more hydrogen ions are present.

For the analysis of *calcium hypophosphorosum*, 1.5 gram is dissolved to 100 c.c., and 5 c.c. of the solution are allowed to remain with 200 c.c. of water, 50 c.c. of *N*/10 iodine solution, and 5 c.c. of dilute sulphuric acid in a stoppered bottle for 12—15 hours in the dark. Sodium hydrogen carbonate is then added a little at a time, about $\frac{1}{2}$ -gram being added after the evolution of carbon dioxide has ceased, and the mixture is allowed to remain for 2 hours more. It is then titrated with *N*/10

thiosulphate, of which not more than 15.5 c.c. should be required (theory 14.7 c.c.).

Free hypophosphorous acid was examined by oxidising, and determining the total phosphoric acid formed; also by digestion with iodine, first in acid solution, then in presence of alkali hydrogen carbonate. It was found to contain 8 per cent. of phosphorous acid to 92 of hypophosphorous acid.

Phosphatic acid, the syrupy liquid formed when phosphorus is allowed to remain in moist air, was found to contain phosphoric acid, 55.7 per cent.; phosphorous acid, 25.9; hypophosphorous acid, 1.7; and water, 16.7 per cent.

Sodium hypophosphate was prepared by oxidising phosphorus with dilute nitric acid and silver nitrate (Philipp, Abstr., 1883, 1052). When 20 c.c. of a 0.8 per cent. solution of it is boiled with 10 c.c. of 25 per cent. hydrochloric acid and the liquid neutralised with sodium hydrogen carbonate and allowed to remain for 1 hour with 25 c.c. of $N/10$ iodine solution, the iodine used corresponds with 2I for each $H_4P_2O_6$ present, which may mean that hypophosphoric acid has the constitution $PO(OH)_2 \cdot PO(OH)_2$; and has been hydrolysed to $PO(OH)_3 + PHO(OH)_2$.
C. F. B.

The Gutzeit Mercuric Chloride Test for Arsenic. AUGUST GOTTHELF (*J. Soc. Chem. Ind.*, 1903, 22, 191—193).—A synopsis of the literature concerning this method, together with an account of experimental work to determine the sensitiveness of the test, the work being done in connection with the revision of the United States Pharmacopœia. The Marsh-Berzelius method is acknowledged to be the most accurate of all, but is rather too complicated for general use. It was found best to perform the Gutzeit test in a small flask of 60 c.c. capacity, in the narrow neck of which were placed two plugs of absorbent cotton, the upper one having been previously soaked in a 25 per cent. solution of lead acetate and dried. Two grams of granulated zinc and 20 c.c. of 8 per cent. hydrochloric acid were used in each test, the mercuric chloride paper being placed over the mouth of the flask as usual. 0.001 mg. of arsenious oxide could be detected in 30 minutes. Arsenic acid should always be reduced by means of sulphurous acid or hydriodic acid before applying the test.

W. P. S.

New Colour Reactions with Boric Acid. CHARLES E. CASSAL and HENRY GERRANS (*Chem. News*, 1903, 87, 27).—The ash of the substance to be tested is treated with a few drops of (1) dilute hydrochloric acid, (2) a saturated solution of oxalic acid, and (3) an alcoholic solution of curcumin or turmeric; the mixture is dried on a water-bath and treated with alcohol. In the presence of boric acid, even in small quantity, an intense magenta coloration is produced which is permanent for several hours, although it fades gradually in time and is destroyed by excess of water. The colouring matter is soluble in alcohol or ether and is changed to a rose colour by alkalis. Large amounts of potassium or sodium salts interfere with the formation of the colour, so that, when very small quantities of boric acid are in question,

the substance should be rendered alkaline by the use of a solution of barium hydroxide before the evaporation for incineration.

D. A. L.

Colorimetric Process for the Estimation of Boric Acid. CHARLES E. CASSAL and HENRY GERRANS (*Chem. News*, 1903, 87, 27—28).—The colour reaction for boric acid (preceding abstract) can be applied quantitatively. In the case of milk, 15 to 20 grams are rendered strongly alkaline with a solution of barium hydroxide and evaporated to dryness in a platinum dish at 105°. The residue is well charred, broken up, then acidified with hydrochloric acid, and treated with successive small quantities of water and filtered. The filter and contents, rendered alkaline with barium hydroxide, are carefully ignited and dissolved in a small quantity of 25 per cent. hydrochloric acid, this solution and the filtrates are mixed and made up to 100 c.c. Ten c.c. of this solution are mixed with 10 to 15 grams of purified sand, made alkaline with a solution of barium hydroxide, and occasionally stirred while being evaporated to dryness. The dry mass is just acidified with 25 per cent. hydrochloric acid and mixed with 2 c.c. of a saturated solution of oxalic acid and 2 c.c. of an alcohol solution of curcumin (containing 1 gram per litre); the mixture is dried, but to intercept any boric acid volatilised it is covered with a funnel, to the stem of which is attached a set of potash bulbs containing barium hydroxide solution and immersed in cold water; through this, air is gently aspirated. When dry, an additional c.c. of curcumin solution is mixed with the sandy mass, which is again taken to dryness and then treated with successive quantities of alcohol or methylated spirit. The contents of the potash bulbs are poured on to the sand, then rendered alkaline, treated with the various reagents, and also dried and extracted with alcohol or spirit. The combined alcoholic solutions are filtered and the boric acid determined colorimetrically by comparison with a solution of known strength.

D. A. L.

Use of Ferric Potassium Chloride for the Solution of Steel in Making the Estimation of Carbon. GEO. W. SARGENT (*J. Amer. Chem. Soc.*, 1902, 24, 1076—1079).—The solution of ferric potassium chloride is prepared by dissolving 267 grams of ordinary ferric chloride (which usually contains 51·5 per cent. of actual ferric chloride) and 130·7 grams of potassium chloride in 1 litre of water. The drillings are dissolved in this solution, which contains sufficient free acid to prevent the formation of any basic salt. Should hydrogen be evolved, the acidity of the solution must be diminished by partial neutralisation. The filtrate from the carbon may be chlorinated and employed for dissolving a second lot of drillings, after adding the requisite quantity of potassium chloride to form the double salt.

W. P. S.

Estimation of Atmospheric Carbon Dioxide by the Walker Method. A. G. WOODMAN (*J. Amer. Chem. Soc.*, 1903, 25, 150—161).—In ordinary circumstances, Walker's method (compare Trans.,

1900, 77, 1110) was found to be accurate to 0.1 part of carbon dioxide in 10,000, and, with careful attention to details, even to 0.03 part. With large amounts of carbon dioxide, say 40 parts, it was found advisable to employ a smaller volume of air so as to avoid using an undue quantity of barium hydroxide solution. The method is considered preferable to that of Pettenkofer.

W. P. S.

Use of Anhydrides and Chloro-anhydrides in Alkalimetry.
 BERNARDO ODDO (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 58—64).—The author has experimented with acetic anhydride, acetyl chloride, phosphorus oxychloride, sulphuryl chloride, and phosphorus trichloride in order to determine whether they can be made use of in the preparation or control of standard alkali solutions. All these compounds give good results, and, as they are readily purified, they offer great advantages over such substances as sodium carbonate and oxalic acid. Special recommendation is made of phosphorus trichloride, which reacts with sodium hydroxide solution according to the equation: $\text{PCl}_3 + 5\text{NaOH} = 3\text{NaCl} + \text{Na}_2\text{HPO}_3 + 2\text{H}_2\text{O}$; the equivalent of the trichloride is therefore 27.47. After distilling twice and collecting the fraction boiling at 74—75°, a slight excess of the trichloride is added to a 50 c.c. flask with ground stopper containing 25 c.c. of the alkaline solution to be tested, the total tare of which has been determined; on weighing again, the weight of the trichloride taken is obtained. The alkaline solution is then run in from a burette until the liquid is neutral to phenolphthalein, the strength of the alkali solution being then easily calculated. Working in this way, standard alkali solution can be prepared in a couple of hours.

T. H. P.

Chemical Method for Determining the Quality of Limestone.
 ALFRED M. PETER (*J. Amer. Chem. Soc.*, 1903, 25, 143—150).—From the results of his experiments, full details of which are given, the author considers that a limestone which absorbs much more than 0.3 per cent. of oxygen, and at the same time contains as much as 1 per cent. of phosphoric acid (P_2O_5), especially if it contains also several per cent. of clay, will disintegrate rapidly on exposure to air and moisture, and is undesirable for road-making. The amount of oxygen absorbed is estimated as follows: 1 gram of the finely powdered sample, dried at 100°, is weighed into a flask, 25 c.c. or more of *N*/10 potassium permanganate solution and 100 c.c. of 10 per cent. sulphuric acid added, and the flask shaken. Two other flasks are also charged with the same amounts of permanganate and sulphuric acid to serve as checks on the decomposition of the permanganate due to heat and acid alone. All the flasks are then placed on a boiling water-bath for 30 minutes, after which 30 c.c. or more of *N*/10 oxalic acid solution are added, and the flasks heated a few minutes longer, until all brown manganic compounds have disappeared. The excess of oxalic acid is then titrated back with the permanganate solution.

W. P. S.

Estimation of Zinc as Sulphide. ALFRED THIEL and A. M. KIESER (*Zeit. anorg. Chem.*, 1903, 34, 198—201. Compare this vol., ii, 105).—For the estimation of zinc in a solution which contains no other metal, it is sufficient to add ammonia until the precipitate at first formed is redissolved, then excess of ammonium sulphide, and evaporate to dryness. The zinc sulphide is carefully ignited in a current of hydrogen sulphide. Results are given which show the exactness of the method. Provided that the heating be carried out carefully, there is no fear of any loss of zinc salt during the volatilisation of the ammonium salts. J. McC.

Electrolytic Precipitation of Zinc and Copper. EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1902, 24, 1073—1076).—For the electrolytic deposition of copper, the following conditions are found to give the best results: potassium zinc sulphate solution, containing 0.2002 gram. of zinc; sodium acetate, 1 gram; acetic acid (99 per cent.), 0.3 c.c.; total dilution, 150 c.c.; cathode surface, 100 sq. cm.; *N.D.*₁₀₀, 0.36 to 0.70 ampere; voltage, 4 to 5; temperature, 65°; and time, 2 hours. The anode should consist of a flat platinum spiral and the cathode of a platinum basin, on the inner surface of which is deposited a silver coating. After 1 hour, the solution appears full of bubbles. At this stage, a few drops of ammonia are added and the action of the current continued for a further 50 minutes. The solution is then siphoned off and the deposit washed with water, alcohol, and ether. The method is also useful for the estimation of zinc in blends.

Copper may be estimated in chalcopyrite by decomposing the latter in the usual way, evaporating to dryness, dissolving the residue in a little dilute sulphuric acid, and proceeding with the electrolysis under the following conditions: total dilution, 150 c.c.; concentrated sulphuric acid, 10 c.c.; temperature, 60° to 70°; *N.D.*₁₀₀, 0.8 to 1 ampere; voltage, 2 to 3; time, 1 hour and a half. The solution from the copper deposit is then nearly neutralised with ammonia, and, after the addition of ammonium oxalate, the iron precipitated with a current of *N.D.*₁₀₀ = 0.5 to 1 ampere and 2 to 3.5 volts at a temperature of 40° to 60°. W. P. S.

Copper Assay by the Iodide Method. ALBERT H. LOW (*J. Amer. Chem. Soc.*, 1902, 24, 1082—1086).—0.5 gram of copper ore is evaporated nearly to dryness with 6 c.c. of nitric acid. Five c.c. of hydrochloric acid and 6 c.c. of sulphuric acid are then added, and the heating continued until fumes of sulphuric acid are evolved. After cooling, 25 c.c. of water are added, the solution is boiled, filtered, and the copper precipitated in the filtrate by introducing a strip of aluminium and 1 drop of hydrochloric acid and boiling for 10 minutes; 15 c.c. of hydrogen sulphide water are then added, the copper is collected in a filter, quickly washed, and dissolved by pouring 5 c.c. of a mixture of equal volumes of nitric acid and water over the aluminium strip and filter; 5 c.c. of saturated bromine water are now poured on to the filter, which is finally washed with hot water. The filtrate is boiled to expel excess of bromine, a slight excess of ammonium hydroxide is

added, and after again boiling the solution is acidified with acetic acid; 3 grams of potassium iodide are then introduced and the liberated iodine titrated with sodium thiosulphate solution, the titer of which is ascertained by titrating a solution of pure copper foil treated as above mentioned. Starch solution is added as indicator, and, towards the end of the titration, the thiosulphate solution is added drop by drop until the faint lilac colour permanently disappears. Zinc and silver have no influence on the method, neither have lead, bismuth, arsenic, or antimony.

W. P. S.

Estimation of Mercury. CHARLES J. PRETZFELD (*J. Amer. Chem. Soc.*, 1903, 25, 198—209).—The following methods were found to give the most accurate results: (1) precipitation as mercurous chloride by reduction with phosphorous acid or a mixture of phosphorous acid and hydrogen peroxide in the presence of sodium chloride; (2) precipitation as arsenate; (3) precipitation electrolytically. The separation of mercury from arsenic, antimony, and copper by the use of tartaric acid and potassium cyanide was found to be more complete, and consequently more accurate, than by the use of ammonium sulphide. To a solution containing these metals, tartaric acid is added, then an excess of potassium cyanide, and hydrogen sulphide passed through the solution to saturation.

W. P. S.

Testing Sublimate-dressings. GUSTAV FRERICHs (*Chem. Centr.*, 1903, i, 251—262; from *Apoth. Zeit.*, 17, 834).—Five grams of the material are placed in a funnel and slowly drenched with dilute ammonium sulphide (1:1). The mass is then washed first with water, then with very dilute hydrochloric acid, and then again with water. It is then pressed out with the fingers, transferred to a wide-mouthed bottle, and treated with 15—25 c.c. of *N*/10 iodine. After closing the flask for some time, 200 c.c. of water are added and the excess of iodine is titrated as usual. One c.c. of iodine solution absorbed, represents 0.01355 gram of mercuric chloride.

To see whether the mercury is equally distributed, the material is spread out on a plate and moistened with weak ammonium sulphide, when the colour should be uniform.

L. DE K.

Conditions for the Estimation of Manganese in Acid Solution by means of Persulphates. HENRI BAUBIGNY (*Compt. rend.*, 1903, 136, 449—451. Compare this vol., ii, 184).—By means of ammonium persulphate, manganese is completely precipitated as peroxide from a solution containing up to 5.5 per cent. of sulphuric acid. The mixture should be boiled for not longer than 20 minutes. The quantity of persulphate necessary increases with the concentration of the sulphuric acid. In presence of nitric acid, the mixture must be boiled for a longer time and the precipitation is not quite so complete.

J. McC.

Application of the Theory of Galvanic Cells to the Quantitative Separation of Metals. AUGUSTE HOLLARD (*Bull. Soc. chim.*, 1903, 29, iii, 116—122).—The method is suitable for the separation

The glycerol is estimated in the distillate by titration with potassium dichromate and sulphuric acid. The results of the experiments show that the method is accurate to about 5 per cent., the amount of glycerol found being as a rule too high.

K. J. P. O.

Estimation of Phenols in Drugs. ÉTIENNE BARRAL (*J. Pharm. Chim.*, 1903, [vii], 17, 98—100).—The drug is distilled with dilute hydrochloric acid when the phenols pass over with the steam. The solid phenols are weighed as such and the amount of dissolved compounds determined by conversion into bromophenols and estimation of bromine in the weighed precipitate. When phenol ethers are present, they are hydrolysed by alcoholic potassium hydroxide before distillation.

G. D. L.

Reactions of Guaiacol. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1903, [vii], 17, 173—174).—The author gives two new reactions for guaiacol.

Aqueous solutions of guaiacol mixed with a solution containing 1 or 2 per cent. of chromic acid give a brown liquid and brown precipitate. If, instead of chromic acid, iodic acid is used, the liquid turns orange-brown and an orange-red precipitate is formed resembling kermes mineral.

L. DE K.

Assay of Creosote by means of Glycerol and Water. R. MICHONNEAU (*J. Pharm. Chim.*, 1903, [vii], 17, 161—164).—Fifteen c.c. of creosote are put into a graduated tube; 5 c.c. of glycerol are added, and the whole mixed by shaking. The tube is now filled with water up to the 50 c.c. mark and thoroughly shaken; after the layers have separated, the aqueous layer is removed and the shaking with water is twice repeated. After the third shaking, the volume of the creosote is read off. Pure creosote will now be found to measure 14 c.c., but if it contained an addition of 10 per cent. of phenol the volume will be 13.5 c.c. A sample containing 20 per cent. of phenol yields 13 c.c., and one containing 40 per cent. 12 c.c., of undissolved liquid.

L. DE K.

Removal of Mercury from Saccharine Liquors after Treatment with Mercuric Nitrate. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1903, [vii], 17, 5—7).—Mercuric nitrate is often the only reagent capable of removing optically active nitrogenous compounds, the presence of which prevents the detection of sugars, in physiological investigations. After treatment of the solution with mercuric nitrate and neutralisation, the excess of mercury is removed by agitation with zinc dust, and sugars determined after making the clear solution alkaline.

G. D. L.

Detection of Small Quantities of Maltose in the Presence of Glucose. LÉON GRIMBERT (*J. Pharm. Chim.*, 1903, [vii], 17, 225—228).—Twenty c.c. of the solution containing the two sugars are treated with 1 c.c. of phenylhydrazine and 1 c.c. of glacial acetic acid. After heating on a boiling water-bath for 1 hour, the mixture

is allowed to cool, the osazones formed are collected on a filter, washed with cold water, dried, extracted with benzene until the extract is colourless, and again dried at 100°. The purified osazone is then triturated with the smallest possible quantity of an equal mixture of acetone and water and filtered. The filtrate soon deposits crystals of maltosazone. An alternative method consists in boiling the purified osazones with a little water for 5 minutes, filtering rapidly, and allowing the filtrate to cool and deposit crystals of maltosazone. Either method is stated to be capable of detecting maltose in a solution containing 1 per cent. of dextrose and 0.05 per cent. of maltose.

W. P. S.

Estimation of Stearic Acid. HANS KREIS and AUGUST HAFNER (*Zeit. Nahr.-Genussm.*, 1903, 6, 22—27).—The method described by Hehner and Mitchell (*Abstr.*, 1897, ii, 289) was found to give trustworthy results provided that not less than 0.5 gram of the mixed fatty acids is taken for the estimation. With smaller quantities, there is a danger of supersaturation taking place with a result that no stearic acid is obtained. Both palmitic and stearic acids were found to be less soluble in alcohol than stated by Hehner and Mitchell, but ethyl alcohol was used, whilst the latter employed rectified alcohol from methylated spirit in their investigations. The method is considered to be of use for the detection of margarin in butter, as the latter was found to contain only very small amounts of stearic acid.

W. P. S.

Reaction of Cacodylic Acid and the Cacodylates. J. BOUGAULT (*J. Pharm. Chim.*, 1903, [vii], 17, 97—98).—When left in contact in the cold in a closed tube with a hydrochloric acid solution of hypophosphorous acid, cacodylates develop a distinct odour of cacodyl, and no deposition of arsenic occurs unless much cacodylate is used, when arsenic separates very slowly. Methylarsinates do not give a cacodylic odour, the whole of the arsenic being set free, and do not prevent the reaction with cacodylates, but the presence of the latter in quantity retards the separation of arsenic from them. In a 12 hours' test, 0.1 mg. of cacodylate can be detected in methylarsinates, and in a similar manner an admixture of less than 0.1 mg. of arsenious or arsenic acid in sodium cacodylate is revealed.

G. D. L.

Composition of Cow's Milk. H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1903, 25, 132—142).—Monthly analyses, extending over 2 years, of the milk of one herd of cattle containing 600 head showed the percentage of proteids, like that of the fat, to vary with the season, being higher in the autumn and winter than in the spring and summer. The percentage of lactose remained nearly constant throughout the year. Generally, the milks rich in fat were also rich in proteids, and in these analyses the excess of the latter above the normal averaged about one-third as much as the excess of fat. The results confirmed the conclusion arrived at by Richmond that any

deficiency in solids not fat is chiefly due to lactose, and any excess above 9 per cent. to proteids. The relation between proteids and ash was found to be expressed by the formula: $A = 0.38 + 0.10P$, closely agreeing with Richmond's formula (compare Abstr., 1902, ii, 182).
W. P. S.

Creaming of Milk During its Sale. WILLIAM FREAR and M. H. PINGREE (*J. Amer. Chem. Soc.*, 1902, 24, 1136—1138).—Two gallons of milk were placed in a deep can, having been first mixed and sampled. At intervals of two hours, samples were taken from the can by means of a pint dipper, the bulk of the milk being disturbed as little as possible. The results of the analyses of the samples showed that the second to sixth portions inclusive contained an undue amount of fat, whilst the last portions consisted of greatly impoverished milk.
W. P. S.

Influence of Feeding with Cottonseed Meal and Sesamé Cakes on the Composition of Butter Fat. A. J. SWAVING (*Zeit. Nahr.-Genussm.*, 1903, 6, 97—115).—The butter from cows fed on cottonseed meal was found to give the characteristic test for cottonseed oil on applying Halphen's reaction, but the feeding did not influence the refractometer number and Reichert-Meissl value of the butter. The substance which gives the coloration can be detected in the butter within 24 hours of the first meal.

Sesamé oil was in no case detected in the butter of cows fed on sesamé cakes, either by Baudouin's or Soltsien's reactions.

W. P. S.

The Bromine Absorption of Oils. PARKER C. McILHINEY (*J. Amer. Chem. Soc.*, 1902, 24, 1109—1114).—The presence of mineral matter, such as lime and the oxides of lead and of manganese, decreases the bromine substitution figure given by oils, and this reduction must be taken into account in the analysis of boiled linseed oil and of driers. From the results of the experiments on the rate of action of bromine dissolved in carbon tetrachloride on rosin, and comparative experiments with Hübl's solution and the same substance, the author considers the bromine absorption of rosin to be a more definite figure than the iodine number. An excess of 100 per cent. of bromine was found to be necessary, in the case of linseed oil, for the absorption to be completed within a short time. The presence of water and variations of the temperature from 0° to 30°, and of the time of action from 88 to 180 minutes, only slightly affect the bromine absorption value of linseed oil.
W. P. S.

Kapok Oil. L. PHILIPPE (*Ann. Chim. anal.*, 1903, 8, 18—23).—This oil, which is suitable for culinary purposes, has given the following constants: sp. gr. at 15°, 0.9237; iodine number, 75.5; free acidity, 5.2 per cent.; Planchon number (soluble acids), 0.37; Koetstörfer (or saponification) number, 196.5; Reichert number (volatile acids), 3.3; Hehner number (fixed fatty acids), 95.4. The insoluble fatty acids,

obtained in the usual manner, showed: melting point, $35.5-35.36^{\circ}$; solidifying point, 31.5° ; saturation number (or number of c.c. of normal potassium hydroxide required to neutralise 5 grams of fatty acid), 12; acetyl number, 86. These acids were found to consist of 30 per cent. of palmitic acid and 70 per cent. of oleic acid containing some proportion of an unidentified acid.

After making the usual correction, it will be noticed that there is a great difference between the amount of potassium hydroxide required for the saponification of the fat (0.1965 gram) and that absorbed by the fatty acids (0.1346 gram); this phenomenon, which may prove useful for the identification of the oil and for its detection in mixtures, is due to the fact that the acids become partly anhydrous.

L. DE K.

The Iodine Number of Sesamé Oil. J. J. A. WIJS (*Zeit. Nahr.-Genussm.*, 1902, 5, 1150—1155).—Thirty-seven samples of this oil were examined by the author, his iodine chloride method being used to estimate the iodine numbers. The "first pressings" gave oils with numbers between 106.1 and 116.8; for the "second pressings," the numbers varied from 105.2 to 110.3, and for the "third pressings" from 103.9 to 109.8. Results published previously by various authors give numbers between 102.7 and 115, as estimated by Hübl's method.

W. P. S.

Estimation of Formaldehyde. HUGO SCHIFF (*Chem. Zeit.*, 1903, 27, 14).—Ten grams of a concentrated sample are diluted to 200 c.c. and carefully neutralised. 0.5 gram of ammonium chloride is dissolved in 3—4 c.c. of water, also neutralised, and mixed with 10 c.c. of the diluted formaldehyde solution. Ammonium sulphate may also be used. The liberated acid is then titrated with normal potassium hydroxide, using litmus as indicator. Two mols. of potassium hydroxide represent three mols. of formaldehyde. The results agree very well with the standard iodometric method.

L. DE K.

Analysis of Vanilla Extract. A. L. WINTON and M. SILVERMAN (*J. Amer. Chem. Soc.*, 1902, 24, 1128—1135).—The following modification of Hess and Prescott's method for the estimation of vanillin and coumarin was found to be satisfactory. Twenty-five grams of the vanilla extract are heated on a water-bath until free from alcohol, then precipitated with normal lead acetate solution, and filtered. After washing the precipitate with a little hot water, the cooled filtrate is methodically extracted with ether, using about 20 c.c. of the latter for each extraction. The vanillin is separated from the combined ether extracts by shaking 4 or 5 times with 2 per cent. ammonia solution. The ethereal solution containing the coumarin is allowed to evaporate spontaneously, dried in a desiccator, and weighed. The dry residue usually consists of pure coumarin, but it is advisable to extract it with light petroleum and deduct the insoluble residue. The coumarin should have a melting point of 67° . The vanillin is obtained from the ammoniacal solution by acidifying with hydrochloric acid and

repeatedly extracting with ether. After evaporating the ether at the ordinary temperature, the residue is dried over sulphuric acid and weighed. The vanillin is then extracted with boiling light petroleum (b. p. 80—85°) and the insoluble residue re-weighed and subtracted from the total weight. Vanillin should melt between 80° and 81°. Experimental results are given and also analyses of commercial extracts. Besides vanillin and coumarin, the total residue (including glycerol), sucrose, glycerol, and alcohol were also estimated in these samples, the usual methods being employed. Some of the extracts were artificially coloured. W. P. S.

Estimation of Hydroxylamine in Oximes and of Phenylhydrazine in Hydrazones and Osazones. SIRO GRIMALDI (*Chem. Centr.*, 1903, i, 97—98; from *Staz. sperim. agrar. ital.*, 35, 738—746).—The oxime, &c., is introduced into a flask with a long, narrow neck and heated with 100 c.c. of standardised hydrochloric acid for one hour in the water-bath. The regenerated aldehyde or ketone is removed (and may be weighed as a control) and the excess of acid titrated with, say, *N*/100 sodium hydroxide. From the amount of acid absorbed, the phenylhydrazine or hydroxylamine is calculated. Good results have been obtained when operating with various oximes, hydrazones, and osazones. L. DE K.

Estimation of Strychnine in Mixtures of Strychnine and Brucine. HARRY M. GORDIN (*Arch. Pharm.*, 1902, 240, 641—644).—Keller's method (*Zeit. Oesterr. Apoth.-Ver.*, 1903, 587) gives results 4 per cent. too low. The reason is that some of the strychnine, as well as all the brucine, is converted by the nitric acid into substances not of a basic character. This source of error is obviated by using a weaker acid and digesting for a shorter time.

About 0.2—0.3 gram of the mixture of alkaloids is dissolved in 15 c.c. of 3 per cent. sulphuric acid with the aid of gentle heat, and to the solution, when it is cold, 3 c.c. of a cold mixture of equal parts of concentrated nitric acid of sp. gr. 1.42 and water is added. After exactly 10 minutes, the whole is poured into a separating funnel, aqueous sodium hydroxide is added until the liquid is strongly alkaline and a turbidity of strychnine has formed, and the mixture is then shaken three times with chloroform, which extracts strychnine, but not brucine. The chloroform solution is filtered through a double filter into a small tared flask, 2 c.c. of amyl alcohol are added, and the liquid is distilled off, the last traces being removed by a current of air led over the mouth of the flask (not into it) while the latter is standing in a water-bath. Finally, the flask is dried for about 2 hours at 135—140° and weighed. The maximum error in 3 estimations was 0.4 per cent. of the total quantity of strychnine.

Sodium hydroxide is preferred to ammonia for liberating the alkaloid, as by its use the base is obtained colourless. It is better to use chloroform for the extraction instead of chloroform-ether, because the latter dissolves some water and with it traces of alkali. The addition of a little amyl alcohol to the chloroform solution prevents alkaloid from being carried over by decrepitation during the distillation

of the liquid. The alkaloid can be titrated instead of being weighed, *N/40* acid being used with hæmatoxylin as the indicator; the result is not more accurate, but the drying is obviated. C. F. B.

Estimation of Urea in Blood. JOSEPH BARCROFT (*J. Physiol.*, 1903, 29, 181—187).—A modification of the hypobromite method is described, by means of which an estimation of urea in 1 or 2 c.c. of blood may be made. The proteids are removed previously by means of alcohol. W. D. H.

The Amount of Urea in Normal Human Urine and its Estimation. WM. OVID MOOR (*Zeit. Biol.*, 1902, 44, 121—160).—The Liebig-Pflüger method is not available for the estimation of the total nitrogen in urine, for although the barium and silver precipitate contains the xanthine bases, urochrome and hæmatoporphyrin, only a part of the uric acid, thiocyanate, and pigments are precipitated. Other methods give somewhat similar results. In the present research, the urea was extracted with alcohol; the extract decomposes at the ordinary temperature more than half its weight of potassium permanganate. This easy oxidisability of the alcoholic extract cannot be explained by the presence of urea, uric acid, hippuric acid, or creatinine; the easily oxidisable substance can be separated from urea by amyl alcohol, in which it is insoluble. After oxidation of neutral urine with zinc permanganate, the urea can be extracted by ethyl-amyl alcohol free from impurities. The urea in this can be estimated by titration with mercuric chloride, potassium hydroxide in amyl alcohol serving as indicator. Further details on the actual amount of urea are promised. W. D. H.

Identification of Pyramidone. G. RODILLON (*J. Pharm. Chim.*, [vii], 17, 172—173).—Pyramidone (dimethylaminodimethyloxyquinizine) turns blue when its aqueous solution is mixed with gum arabic and exposed to the air. The author finds that this reaction may also be obtained by other means.

0.1 gram of the substance is dissolved in 5 c.c. of water and a drop of solution of sodium hypochlorite is added, when a fine blue colour will develop. As an excess of hypochlorite is harmful, it is better to use hydrogen peroxide, but then it is necessary to heat to about 60° or 70°. Perhaps a colorimetric estimation may be based on this reaction. With pyramidone, ferric chloride develops, an intense violet colour analogous to that given by phenols. L. DE K.

Estimation of Mustard Oil. A. SCHLICHT (*Zeit. öffentl. Chem.*, 1903, 9, 37—41).—Twenty-five grams of the powdered mustard seeds are digested for 4 hours with cold water and then boiled for 15 minutes, the flask in which the digestion and boiling is carried out being connected with an absorption flask containing an alkaline solution of permanganate. After completely cooling, a solution of myrosin is added and allowed to act for 16 hours at the ordinary temperature. An alternative method is to digest 25 grams of the powdered seeds in 300 c.c. of water containing 0.5 gram of tartaric acid for 16 hours at

the ordinary temperature, the flask in this case also being connected to an absorption apparatus. In both methods, the contents of the digestion flasks are then subjected to distillation and the mustard oil oxidised and estimated as usual.

W. P. S.

Estimation of Digitalin in Official Preparations of Digitalis and Digitalin. ECALLE (*J. Pharm. Chim.*, 1903, [vii], 17, 228—232).—In the case of the tincture, 100 c.c. are evaporated to 10 c.c. and diluted to 100 c.c. with water. This solution is precipitated with normal lead acetate and the volume made up to 200 c.c. After shaking and filtering, 100 c.c. of the filtrate are precipitated with 10 c.c. of sodium sulphate solution and the lead sulphate allowed to settle completely. Ninety c.c. of the clear solution are then decanted off, rendered ammoniacal, and extracted with five successive quantities of chloroform. The latter is evaporated from the united extracts and the residue obtained dissolved in 3 c.c. of chloroform. Ten c.c. of ether and 70 c.c. of light petroleum are added, the mixture is cautiously stirred, and placed aside for 48 hours. The clear solution is then decanted, and the residue dried and weighed.

W. P. S.

Physiologico-chemical Notes. EDUARD SCHAEER (*Zeit. anal. Chem.*, 1903, 42, 1—10).—I. *The Biuret Reaction.*—In the production of the biuret reaction, other copper salts than the sulphate may be used, and various substances may take the place of the alkali hydroxides. Barium and calcium hydroxides, sodium carbonate, phosphate, nitrite, and borate, magnesia, basic lead acetate, aluminium acetate, ammonia, coniine, trimethylamine, triethylamine, piperidine, morphine, strychnine, aniline, diphenylamine, antipyrine, glycine, and urea are all effective. Although some of these substances possess a very feeble alkaline character, the presence of an alkaline substance seems to be necessary, since the reaction is not produced by the simple oxidation of a proteid in the presence of a copper salt.

II. *Trommer's Sugar Reaction.*—In this reaction, also, the alkali hydroxide may be replaced by substances of feeble alkalinity, such as magnesia, borax, lead acetate, coniine, nicotine, piperidine, and triethylamine, but salts, such as sodium salicylate, phosphate, and nitrite, and aluminium acetate, which yield an alkali by hydrolytic dissociation, do not produce the reaction, neither do aniline, acetanilide, antipyrine, glycine, or urea, or substances of non-alkaline character. The copper salts of organic acids are very readily reduced.

III. *Detection of Blood Stains.*—Aloin, with an oxidising agent, yields a red colour with blood, which is both more intense and more permanent than the guaiacum-blue. The reaction is best performed in a concentrated (70—75 per cent.) solution of chloral hydrate, in which even old blood stains dissolve readily. This solution is treated with a little aloin and the mixture covered with a layer of hydrogen peroxide or ozonised oil of turpentine (compare Abstr., 1902, i, 168).

M. J. S.

General and Physical Chemistry.

Method for Determining the Index of Refraction of Solid Hydrocarbons with the Pulfrich Refractometer. Index of Refraction of the Solid Hydrocarbons in Petroleum. CHARLES F. MABERY and LEE SHEPHERD (*Amer. Chem. J.*, 1903, 29, 274—281).—A method is described for adapting the Pulfrich refractometer to the determination of the index of refraction of substances which are solid at the ordinary temperature. The required temperature is obtained by passing an electric current through two coils of German silver wire, one of which surrounds the glass cup, whilst the other is placed within the cup. The determinations were made by the method of mixtures, the solvent employed being a petroleum distillate boiling at 202—203° under 50 mm. pressure, and consisting essentially of the hydrocarbon, $C_{18}H_{38}$. The sp. gr. is in all cases referred to water at 4°.

The following results were obtained with the hydrocarbons isolated from Pennsylvania petroleum (Mabery, *Abstr.*, 1902, i, 733). The hydrocarbon, $C_{23}H_{48}$, boiling at 260—262° under 50 mm. pressure, has a sp. gr. 0.7769 and n_D 1.4432 at 60°, and sp. gr. 0.7709 and n_D 1.4260 at 70°. The hydrocarbon, $C_{24}H_{50}$, boiling at 272—274° under 50 mm. pressure, has a sp. gr. 0.7771 and n_D 1.4432 at 60°, and sp. gr. 0.7719 and n_D 1.4251 at 70°. The hydrocarbon, $C_{25}H_{52}$, boiling at 282—284° under 50 mm. pressure, has a sp. gr. 0.7765 and n_D 1.4241 at 70°, and sp. gr. 0.7632 and n_D 1.4212 at 80°. The hydrocarbon, $C_{26}H_{54}$, boiling at 292—294° under 50 mm. pressure, has a sp. gr. 0.7780 and n_D 1.4320 at 70°, and sp. gr. 0.7685 and n_D 1.4305 at 80°. The hydrocarbon, $C_{27}H_{56}$, boiling at 300—301° under 50 mm. pressure, has a sp. gr. 0.7757 and n_D 1.4206 at 70°, and sp. gr. 0.7655 and n_D 1.4194 at 80°. The hydrocarbon, $C_{28}H_{58}$, boiling at 312—314° under 50 mm. pressure, has a sp. gr. 0.7770 and n_D 1.4184 at 70°, and sp. gr. 0.7669 and n_D 1.4170 at 80°.

The following values were obtained with hydrocarbons separated from commercial paraffin wax. The hydrocarbon, $C_{23}H_{48}$, boiling at 260—262° under 50 mm. pressure, has a sp. gr. 0.7706 and n_D 1.4256 at 60°, and sp. gr. 0.7641 and n_D 1.4374 at 70°. The hydrocarbon, $C_{25}H_{52}$, boiling at 282—286° under 50 mm. pressure, has a sp. gr. 0.7779 and n_D 1.4206 at 60°, and sp. gr. 0.7707 and n_D 1.4194 at 70°. The hydrocarbon, $C_{27}H_{56}$, boiling at 300—302° under 50 mm. pressure, has a sp. gr. 0.7770 and n_D 1.4287 at 70°, and sp. gr. 0.7669 and n_D 1.4276 at 80°. The hydrocarbon, $C_{28}H_{58}$, boiling at 312—314° under 50 mm. pressure, has a sp. gr. 0.7806 and n_D 1.4285 at 70°, and sp. gr. 0.7699 and n_D 1.4226 at 80°.

Commercial paraffin wax itself furnished the following results: sp. gr. 0.7788 and n_D 1.4340 at 60°, and sp. gr. 0.7732 and n_D 1.4311 at 70°.

E. G.

Bunsen Flame Spectrum of Radium. CARL RUNGE and J. PRECHT (*Ann. Physik*, 1903, [iv], 10, 655—657. Compare Giesel, this vol., ii, 20).—A list is given of all the lines observed in the flame spectrum of radium bromide. The strongest and most permanent is the blue line 4826.

J. C. P.

Position of Radium in the Periodic System according to its Spectrum. CARL RUNGE and J. PRECHT (*Phil. Mag.*, 1903, [vi], 5, 476—481. Compare preceding abstract).—Runge and Paschen have shown that the lines of each of the related elements magnesium, calcium, strontium, and barium may be grouped in three pairs; the distance as measured on the scale of frequency between the two lines of each pair is the same for one element, but increases regularly with the atomic weight. The authors have extended the application of this rule to the case of radium.

The rule regarding the variation of the line distance with the atomic weight is thus formulated: the logarithms of the atomic weights and those of the distances when plotted as co-ordinates lie on a straight line for a chemically related group of elements. When this straight line has been found for magnesium, calcium, strontium, and barium, it is then possible by an extrapolation to calculate the atomic weight of radium; the value thus obtained is 258, considerably above the value 225 given by Madame Curie.

J. C. P.

Heat spontaneously developed by Salts of Radium. PIERRE CURIE and A. LABORDE (*Compt. rend.*, 1903, 136, 673—675).—When a thermoelectric couple junction is immersed in a barium chloride containing $\frac{1}{6}$ of its weight of radium chloride and this compared with a similar junction in pure barium chloride, the former indicates a temperature higher by 1.5° than the latter. The quantity of heat developed was measured by a Bunsen calorimeter. The radioactive barium chloride was kept in a tube in melting ice for some time, then introduced into the calorimeter. The mercury moved along the capillary tube quite regularly (2.5 cm. per hour) and stopped when the salt was removed from the calorimeter. The results obtained indicate that 1 gram of radium develops a quantity of heat of the order of 100 calories per hour; for a gram-atom per hour, the development would be 22,500 calories, which is comparable with the heat developed by the combustion of a gram of hydrogen.

This continuous development of heat cannot be explained by an ordinary chemical transformation. It may be due to an internal transformation resulting in a modification of the radium atom itself, or it may be explained by assuming that the radium is able to utilise an external energy of as yet unknown nature.

J. McC.

Experiments with Radium Bromide. F. N. INDRICKSON (*J. Russ. Phys. Chem. Soc.*, 1903, 35, ii, 149—154).—If a barium platino-cyanide screen is arranged to catch the light from a capsule containing 50 mg. of radium bromide placed between the poles of a powerful electromagnet, it is found that, when the current is turned on, the

light is displaced and only gradually returns to its original position when the current is broken. This action was recorded photographically. The effect produced by the action of the light from radium bromide on the electric spark is similar to that brought about by increasing the distance between the discharge knobs. T. H. P.

Radioactivity of Uranium. ERNEST RUTHERFORD (*Phil. Mag.*, 1903, [vi], 5, 441—445).—As shown by Becquerel (*Abstr.*, 1902, ii, 117), uranium preparations that have been rendered inactive (see Becquerel, *Abstr.*, 1900, ii, 518; Crookes, *ibid.*, 586) gradually recover their activity, whilst the precipitates in which the activity was concentrated gradually lose it. By experiments lasting over 160 days, the author shows that the recovery and decay of activity in the case of uranium and uranium X respectively follow the same laws as the recovery and decay of activity in the case of thorium and thorium X (see Rutherford and Soddy, *Trans.*, 1902, 81, 838—842). The activity of uranium X decays nearly in a geometrical progression with the time, and reaches half its initial value in about 22 days. J. C. P.

Comparative Study of the Radioactivity of Radium and Thorium. ERNEST RUTHERFORD and FREDERICK SODDY (*Phil. Mag.*, 1903, [vi], 5, 445—457).—In their radioactive properties, radium and thorium are closely allied; both produce radioactive emanations, and these in turn excite activity on surrounding objects. There is a marked difference, however, in the rate at which the activity of the emanation decays, the intensity of the thorium emanation falling to half its value in one minute, that of the radium emanation in about four days. On the other hand, the excited activity due to radium decays much more rapidly than that produced by thorium.

A detailed examination of the rate of decay for the radium emanation has shown that the same exponential law is applicable here as in other cases (compare Rutherford and Soddy, *Trans.*, 1902, 81, 841—842; Rutherford, preceding abstract; also Curie, this vol., ii, 50).

In the solid state, radium compounds are practically non-emanating, but heat and solution, as in the case of thorium compounds, increase the emanating power. It is now shown that for both radium and thorium the production of emanation takes place at the same rate in a solid, non-emanating compound as in the solution; whilst in the former case, however, the emanation is occluded, in the latter case it escapes as fast as it is formed. This result is favourable to the view that helium is possibly an ultimate disintegration product of a radioactive element, since it is found occluded only in radioactive minerals. When a current of air is passed through a solution of radium chloride, the radioactivity of the salt obtained from the solution by evaporation gradually diminishes, and ultimately reaches a minimum value, unaffected by further aspiration of air; this minimum value represents the non-separable activity. Radium chloride, obtained thus, gradually regains its activity, and the course of the recovery is represented by the equation $I_t/I_o = 1 - e^{-\lambda t}$ (see Rutherford and Soddy, *loc. cit.*). Somewhat similar experiments have been carried out with thorium.

Like thorium and uranium, radium emits both α - and β -rays, the

non-separable activity just referred to consisting of α -rays alone. The radiation of the radium emanation was investigated, and it was found that the radium emanation gives only α -rays, the β -rays appearing only when the emanation has changed into the excited activity. This result supports the view that in all cases the α -rays are first produced, the β -rays being produced in the last stages of the process that can be experimentally traced.

Experiments previously described, relating to the chemical nature of the thorium emanation, have been repeated with that of radium. The radium emanation passes unchanged through phosphoric oxide, sulphuric, nitric, and hydrochloric acids, and over red-hot lead chromate and metallic magnesium. The emanation is not affected by passage through a platinum tube heated almost to fusion. The emanation is not very soluble in water.

J. C. P.

Radioactivity. ERNEST RUTHERFORD (*Phil. Mag.*, 1903, [vi], 5, 481—485).—A reply to certain criticisms of Becquerel and Curie.

J. C. P.

Production of Induced Radioactivity by Actinium. A. DEBIERNE (*Compt. rend.*, 1903, 136, 671—673).—Two plates were placed at an angle over a tube containing an actinium salt. The actuating ions are contained almost exclusively in the tube above the salt, but the plates, nevertheless, become radioactive. This is attributed to an actuating radiation which proceeds from each ion. This radiation is deviated in a magnetic field, and it has been established that the magnetic field does not affect the ions, but only the radiation. The radiation is also deviated by an electric field. The deviation is the same as that which would be found for positively charged particles travelling with a high velocity.

J. McC.

Relationships between Reflective Power and Electrical Conductivity of Metals. ERNST HAGEN and HEINRICH RUBENS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 13, 269—277).—The reflective power of metals for light of wave-length up to 14μ has been determined by the method previously used (*Ann. Physik*, 1902, 8, 432). In all cases, the curve obtained approaches asymptotically the straight line representing total reflection. Using the results obtained with light of wave-length 12μ , it is found that the product of percentage difference between total reflexion and that observed and the square root of the electrical conductivity is constant for all metals; that is, for long waves, the intensity with which light passes into the metal is inversely proportional to the square root of the electrical conductivity. The results are shown to be in agreement with Maxwell's electro-magnetic theory of light.

J. McC.

Alteration of the Dielectric Constant of some Liquids with Temperature. KARL TANGL (*Ann. Physik*, 1903, [iv], 10, 748—767. Compare Ratz, *Abstr.*, 1896, ii, 288).—The author has determined by Nernst's method the dielectric constants of benzene, toluene, *m*-xylene, carbon disulphide, and chloroform from 20° to 180° , and that of ether

to 200° . In the case of the first five liquids, empirical formulæ are obtained which represent closely the variation of the dielectric constant with temperature; this relation for benzene, toluene, and *m*-xylene is very nearly a linear one. The dielectric constant of ether falls rapidly in the neighbourhood of 193.3° , the critical temperature; if the ether is heated above that point to 199° , the dielectric constant falls still further, but on subsequent cooling its value remains constant from 199° to 193.3° . The dielectric constant of ether at the critical temperature is considerably greater than the square of the index of refraction for infinitely long waves, as calculated by Cauchy's dispersion formula.

The Clausius-Mossotti constant is independent of the temperature only in the case of *m*-xylene from 0 — 130° ; for benzene and carbon disulphide, there is an increase to the extent of 5.4 per cent. from 0 — 200° ; there is a decrease of 0.6 per cent. for toluene, from 0 — 100° , of 4.8 per cent. for chloroform from 0 — 60° , of 17 per cent. for ether from 20 — 193° .

J. C. P.

Non-conductivity of Electricity by Metallic Hydrides. HENRI MOISSAN (*Compt. rend.*, 1903, 136, 591—592).—It has been found that the hydrides of potassium, sodium, rubidium, and cesium do not conduct an electric current. The experiments were made with a compact, homogeneous layer 5 cm. long, and this has been found to be the case also when the hydrides are fused.

The author concludes that hydrogen cannot be ranged with the metals nor can the hydrides be regarded as comparable with alloys. In the hydrides, hydrogen behaves like a non-metal.

J. McC.

Formation and Significance of Sodium Alloys in Cathodic Polarisation. M. SACK (*Zeit. anorg. Chem.*, 1903, 34, 286—352).—The author discusses the production of hydrogen in the electrolysis of alkali solutions and concludes that it is formed both primarily and secondarily.

Lead and tin cathodes were polarised in a 3*N*-solution of sodium hydroxide and their potentials measured against a mercury electrode. It was found that the steady evolution of hydrogen from these cathodes is connected with a loosening of the material of the cathode, and this is attributed to the formation of alloys with the sodium. These alloys are then decomposed by the water. When lead and tin are intensely polarised in this solution, a metallic cloud is formed. It has been proved that alloys of these metals rich in silver are decomposed by water with production of this cloud. With lead, the loosening of the metal and steady evolution of hydrogen take place when the cathode potential is about 0.7 volt, and with tin at 0.4 volt, referred to the potential of hydrogen in the same sodium hydroxide solution as zero. The cloud effect in the case of lead is produced at the potential 1.5 volts, and of tin at 1.4 volts, referred to the same standard. Zinc and platinum give rise to no cloud effect, but the metals become loose and porous on the surface. With platinum and lead, the metal is changed to a much greater extent in acid solutions than in solutions of

alkalis. As this change of the metal is due to the action of the cathion, it appears that hydrogen permeates the metal more easily than sodium, and at the same time it definitely proves the secondary character of the hydrogen evolution at the cathode in the electrolysis of alkali hydroxide solutions.

The potential of sodium alloys with lead, tin, and mercury was measured in a methyl alcohol solution of lithium chloride at -80° . The results indicate that the alloy becomes covered with a layer of the pure metal (lead or tin). When the potentials are plotted against the atomic concentrations of sodium in the alloys, the changes in the direction of the curve indicate the existence of the compounds Pb_2Na and Sn_3Na . In the same way, the existence of definite compounds of mercury and sodium are indicated. The results taken together show that these definite compounds are formed during the electrolysis of alkali solutions and are then chemically decomposed by the water present.

Based on the rule that when solids are diluted with solids to produce solid substances the heat change is equal to the free energy, the author has calculated what the potentials of the sodium alloys should be from the heat change and the potential of sodium in the methyl alcohol solution of lithium chloride, and finds values in good agreement with those observed. J. McC.

Theory of the Electrolysis of Solutions of Alkali Chlorides. FRITZ FOERSTER and ERICH MÜLLER (*Zeit. Elektrochem.*, 1903, 9, 171—185, and 195—208).—The authors extend their theory of the chemical action of halogens on alkalis (this vol., ii, 142) to the phenomena which occur at the anode when a solution of an alkali chloride is electrolysed; several of the views put forward in their earlier papers are corrected. The following is a summary of the final conclusions now reached.

When an aqueous solution containing chlorine ions is electrolysed, free chlorine is formed at the anode, $2Cl' + 2F = Cl_2$.

Hypochlorous acid and hypochlorite ions are formed simultaneously, either by the primary reactions $Cl' + OH' + 2F = HOCl$ and $Cl' + 2OH' + 2F = ClO' + H_2O$, or by equilibrium being established between chlorine and water, thus: $Cl_2 + OH' \rightleftharpoons HOCl + Cl'$ and $HOCl + OH' \rightleftharpoons ClO' + H_2O$. As the ratio OH'/Cl' increases (that is, in strongly alkaline or very dilute solutions), the concentration of ClO' will increase.

Hypochlorite is also formed in the mass of the electrolyte from free chlorine and any alkali which may be present.

Since ClO' is more readily discharged than Cl' , hypochlorite cannot reach a very high concentration in the neighbourhood of the anode.

Chlorate is formed from ClO' , when this is discharged at the anode, by the reaction $6ClO' + 3H_2O + 6F = 2ClO_3' + 4Cl' + 6H' + 3O$. It is also formed in the mass of the electrolyte by the secondary reaction $ClO' + 2HClO = ClO_3' + 2H' + 2Cl'$.

The primary formation of chlorate at the anode is always accompanied by an evolution of oxygen; it begins when the con-

centration of ClO' at the anode has reached a value which depends on the anode potential.

The requisite quantity of ClO' may be formed at the anode or may diffuse to it from the surrounding electrolyte. In the latter case (concentrated neutral solutions), chlorate is only formed when the electrolysis has been in progress for some time.

In solutions containing relatively considerable quantities of OH' , oxygen is evolved owing to the anodic discharge of these ions in addition to that due to the discharge of ClO' .

The secondary formation of chlorate only occurs in appreciable amount in solutions containing free hypochlorous acid together with hypochlorite throughout the mass of the electrolyte.

The principal facts which support this theory are:—When concentrated hydrochloric acid is electrolysed, chlorine and traces of oxygen are formed; the quantity of oxygen increases with the dilution of the acid, and chloric acid is formed. In neutral solutions of alkali chlorides, chlorine is the first product found at the anode. The minimum anodic potential at which rapid electrolysis of solutions of hydrochloric acid or of a neutral alkali chloride takes place is the same as that assumed by an indifferent electrode immersed in the solution saturated with chlorine.

In neutral solutions, this minimum value is only obtained with platinised electrodes; smooth electrodes give values at least 0.56 volt higher. In a neutral solution in which the anodic and cathodic products can mix, hypochlorite is formed, and hypochlorous acid is also found at the anode. The concentration of the hypochlorite increases up to a certain value, after which it remains constant, chlorate being formed and oxygen evolved at the anode. The formation of hypochlorite and the beginning of the formation of chlorate do not affect the potential of a platinised anode appreciably when the current density is moderate. The concentration of hypochlorite attained in neutral solutions is higher, the higher the current density and concentration of chloride and the lower the temperature. More hypochlorite is formed with platinised than with smooth anodes. In neutral solutions, except those which are very dilute, about two-thirds of the current produce chlorate and one-third, oxygen at the anode; this is, however, only true when cathodic reduction of hypochlorite is prevented by the addition of chromate. In very dilute solutions, considerably more than one-third of the current is employed in the liberation of oxygen. When carbon anodes are used, the very dilute solutions contained in their pores are electrolysed. If in a neutral solution the cathodic products are prevented from mixing with the anodic products, chlorine is formed at the anode together with oxygen (increasing in quantity as the dilution increases), and the solution surrounding the anode becomes acid with hydrochloric acid, chlorate being formed simultaneously.

In very slightly acid solutions of alkali chlorides, the concentration of hypochlorite attained is smaller, the quantity of oxygen evolved at the anode is smaller, and the yield of chlorate is larger, owing to the secondary formation of chlorate from hypochlorous acid and hypochlorite.

The addition of alkali hydroxide to a solution of a chloride diminishes the concentration of hypochlorite attainable. In a strongly alkaline solution of a chloride, the potential of the anode is determined by the potential required to discharge oxygen from the hydroxide; it increases considerably during the electrolysis. At the lowest potential required to discharge oxygen, mere traces of hypochlorite are produced. As the anodic potential rises, chlorine ions are discharged in greater number, but chlorate is formed rather than hypochlorite. T. E.

Electrolysis of Solutions of Potassium Iodide. FRITZ FOERSTER and K. GYR (*Zeit. Elektrochem.*, 1903, 9, 215—226).—For the electrolysis of a neutral normal solution of potassium iodide, an anodic potential of 0.52 volt (compared with the hydrogen electrode) is required; this is diminished by the addition of alkali hydroxide. Iodine is first liberated at the anode, and, in equilibrium with it, hypiodous acid and hypiodite. In neutral solutions, traces of hypiodous acid exist in equilibrium with small quantities of iodine and hydroxyl ions in the electrolyte, but the main portion of the hypiodite formed is at once converted into iodate. In alkaline solutions, the hypiodite accumulates up to a certain concentration (depending on the concentration, temperature, and current density), which then remains unchanged during the electrolysis, the velocity of its change into iodate being equal to the rate of its formation. In alkaline solutions containing very little iodide, oxygen may be evolved at the anode, especially at higher temperatures and current densities. Periodate is formed only in traces, if at all. T. E.

Electrolytic Reduction of Potassium Chlorate. ANDRÉ BROCHET (*Zeit. Elektrochem.*, 1903, 9, 160—162).—When a solution of potassium chlorate is electrolysed with copper electrodes, potassium chloride is formed; the current efficiency is, however, larger than (it may be double) the theoretical quantity. A brown precipitate containing copper, copper oxide, and basic chloride is also formed. The formation of the precipitate is due to the formation of copper chlorate at the anode; this copper chlorate reacts with the potassium hydroxide formed at the cathode, the oxide so produced being partly reduced to metal by the cathodic hydrogen. The reduction of the chlorate to chloride by copper is a purely chemical reaction which goes on independently of the electrolysis, $\text{Cu}(\text{ClO}_3)_2 + 6\text{Cu} = \text{CuCl}_2 + 6\text{CuO}$. Chlorate is not reduced at all by cathodic hydrogen. T. E.

Electrochemistry of Permanganic Acid. J. K. H. INGLIS (*Zeit. Elektrochem.*, 1903, 9, 226—230).—The changes occurring at an electrode coated with manganese peroxide immersed in a solution of (1) permanganic acid, (2) a manganous salt are: (1) $\text{MnO}_4' + 4\text{H}' = \text{MnO}_2 + 2\text{H}_2\text{O} + 3F$, (2) $\text{MnO}_2 + 4\text{H}' = \text{Mn}'' + 2\text{H}_2\text{O} + 2F$. The potentials, P_1 and P_2 , of these electrodes are represented by $P_1 = P_1' + \frac{RT}{3F} \log \frac{C_{\text{MnO}_4'} \cdot C_{\text{H}'}^4}{C_{\text{MnO}_2} \cdot C_{\text{H}_2\text{O}}^2}$ and $P_2 = P_2' + \frac{RT}{2F} \log \frac{C_{\text{MnO}_2} C_{\text{H}'}^4}{C_{\text{Mn}''} C_{\text{H}_2\text{O}}^2}$, where P_1' and P_2' are the potentials when all the concentrations are unity.

These relations are found to be in agreement with the author's experimental results. Equations (1) and (2) represent stages in the change (3), $\text{MnO}_4' + 8\text{H}^+ = \text{Mn}^{++} + 4\text{H}_2\text{O} + 5F$. A platinum electrode at which this reaction (3) is taking place should have a potential P_3 given by the relation $P_3 \cdot 5F = P_1 \cdot 3F + P_2 \cdot 2F$. For solutions containing $\text{H}_2\text{SO}_4/20 + \text{MnSO}_4/10000$ per litre, $P_2 = 1.602$ volts; $\text{H}_2\text{SO}_4/20 + \text{KMnO}_4/100$ per litre, $P_1 = 1.771$ volts; therefore, for $\text{H}_2\text{SO}_4/20 + \text{MnSO}_4/10000 + \text{KMnO}_4/100$ per litre, P_3 should be 1.703 volts. The actual value found was always larger, and it increased with time. This is due to the oxidation of manganous ions, $2\text{MnO}_4' + 3\text{Mn}^{++} + 2\text{H}_2\text{O} = 5\text{MnO}_2 + 4\text{H}^+$; a calculation shows that the concentration of the Mn^{++} ions in the above-mentioned solution would be reduced to about 10^{-10} .

T. E.

Passivity of Iron and the Periodic Phenomena observed at Iron Electrodes. CARL FREDENHAGEN (*Zeit. physikal. Chem.*, 1903, 43, 1—40).—The author discusses the known facts bearing on the passivity of iron and the various explanations of the phenomenon that have been offered (compare Hittorf, *Abstr.*, 1900, ii, 705; Heathcote, *Abstr.*, 1901, ii, 445; Finkelstein, *Abstr.*, 1902, ii, 81). Some additional experimental work, dealing with the anodic polarisation of iron in various electrolytes, is presented, but the chief object of the paper is to show that all the observed phenomena may be explained by the supposition that iron in the passive condition is protected by a gaseous layer. Iron which has been rendered passive by anodic polarisation in sulphuric acid behaves differently from iron which has been rendered passive by nitric acid, probably because the protecting gaseous layer consists of oxygen in the one case and oxide of nitrogen in the other.

The periodic phenomena observed at iron electrodes (compare Ostwald, *Abstr.*, 1901, ii, 24) are also discussed in the light of the author's explanation.

J. C. P.

Form of the Practical Isothermal in Gaseous Mixtures F. CAUBET (*Zeit. physikal. Chem.*, 1903, 43, 115—117).—A correction applied to some of the author's work on mixtures of methyl chloride and sulphur dioxide (*Abstr.*, 1902, ii, 382), in accordance with Kuenen's criticism (*Abstr.*, 1902, ii, 491).

J. C. P.

Simple Relation between the Molecular Heat of Solidification and the Boiling Point. II. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1903, [vii], 28, 531—574. Compare *Abstr.*, 1901, ii, 641, and this vol., ii, 267).—In order to establish the general validity of the formula $(L + S)/T = Q/T' = (L + S + C)/T' = 30$, where L is the molecular heat of vaporisation, S the molecular heat of solidification, T the boiling point (absolute) under a pressure of 760 mm., Q the heat of formation of a compound, T' the temperature (absolute) at which the dissociation pressure of the compound is 760 mm., and C the specific heat, various substances, elementary and compound, have been examined.

The data necessary for complete verification are only known for the

three compounds, carbon dioxide, ammonia, and water. For carbon dioxide, the most trustworthy values lead to $(L+S)/T' = 32.12$; from the heat of formation and the temperature of dissociation of carbonates, it is found that Q/T' is constant and equal to about 32. The boiling point of ammonia was found to be -32.15° , and its heat of solidification was calculated to be 1.95 Cal.; the value of $(L+S)/T$ is 31.93. Examination of the dissociation of 17 additive compounds of metallic chlorides and ammonia shows that $Q/T' = 32.33$. The additive compounds of methylamine and ethylamine with lithium bromide and chloride give values ranging from 31 to 39 for Q/T' , and the ratios obtained with the ammonio-copper sulphates are also high. For water, the value of $(L+S)/T$ is 29.73, and for various salt hydrates the value of Q/T' is just over 30. The values of T' in the case of the hydrates have mostly been determined by extrapolation and are, therefore, only approximate. It is worthy of note that the value of Q/T' generally exceeds that of $(L+S)/T$ by about one unit.

The following values of $(L+S)/T$ have also been calculated: for bromine, 29.52; for chlorine, 32.21; for iodine, 27.80; for ethylene glycol, 30.84; for trimethylcarbinol, 30.85; for naphthalene, 31.43; for phenol, 29.48; for aniline, 29.92; for benzene, about 28; for nitrobenzene, 28.20; for ethylene bromide, 28.20; for methyl oxalate, 32.27; for chloral, 31.44; for butyric acid, 28.84; for formic acid, 29.86; and for acetic acid, about 32.

The value of $(L+S)/T = 30$ may be made use of for determining the molecular weight from an experimental study of the heat of vaporisation and the heat of solidification.

J. McC.

Molecular Rise of Boiling Point for Nitrobenzene. PAUL BACHMANN and KARL DZIEWOŃSKI (*Ber.*, 1903, 36, 971—974).—The molecular rise in the boiling point for 100 grams of nitrobenzene is 50.1° . The value 46, previously found by Biltz (*Zeit. physikal. Chem.*, 1896, 19, 425), is due to his having used solutions of substances like acetanilide, which did not boil relatively high enough compared with nitrobenzene. Using the value 51.03° as the molecular rise for the maximum dilution, the latent heat of vaporisation of nitrobenzene is calculated to be 89.85 calories.

E. F. A.

Freezing Points of Dilute Solutions. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1903, 25, 291—298).—Besides the common errors of thermometry and of quantitative work in general, in connection with freezing point determinations, the difficulties of experiment are increased by the slowness with which equilibrium is attained. The author describes a method for overcoming the latter difficulty. Since the equilibrium in question is one between two phases, it can be adjusted only on the surface between the two, and, in order to avoid superheating or supercooling, this surface ought to be as large as possible. In the presence of much ice, the equilibrium is obtained with great speed and convenience. Several forms of apparatus are suggested. By a very simple apparatus, it is easy to obtain a depression of half a degree within half a per cent. of its true value. The precautions to be taken, when it is desired to obtain

a result accurate to within less than the thousandth of a degree, are given. Determinations of the depression of the freezing point of potassium chloride solutions were in close agreement with the results of previous workers. The method appears to be sufficiently exact to permit of its being used to standardise thermometers. A. McK.

Point of Maximum Density for Aqueous Solutions of some Organic Substances. WILHELM MÜLLER (*Zeit. physikal. Chem.*, 1903, 43, 109—112. Compare de Coppet, *Abstr.*, 1893, ii, 60; 1895, ii, 343; 1898, ii, 62; 1899, ii, 590; 1900, ii, 529; 1901, ii, 493; 1902, ii, 488).—The organic substances used were phenol, catechol, resorcinol, quinol, pyrogallol, phloroglucinol, mannitol, dextrose, and oxalic, succinic, and tartaric acids. Taking into account also earlier experiments on alcohol and sucrose, the author arrives at the following conclusions. The depression of the temperature of maximum density of water is, for organic substances, dependent not merely on the molecular weight, but also on the constitution. In any given case (alcohol excepted), the depression is approximately proportional to the concentration; the molecular depression tends, however, to increase slightly with the concentration, a variation considered by the author to exceed the experimental errors, and possibly due to a partial association of the dissolved molecules. An increase in the number of hydroxyl groups leads apparently to an increase in the value for the molecular depression; thus the molecular depression for succinic acid is 12.4° , that for tartaric acid is 15.3° , and comparison of the values for the mono-, di-, and tri-hydroxybenzenes shows the same. The molecular depressions produced in dilute solution by the three di-hydroxybenzenes are almost the same, although the tendency for the depression to increase with the concentration is most marked in the case of the ortho-compound. J. C. P.

Physical Properties of the Elements from the Standpoint of van der Waals' Equation of Condition. ISODOR TRAUBE (*Zeit. anorg. Chem.*, 1903, 34, 413—426).—It has already been shown that van der Waals' equation is applicable to the liquid as well as to the gaseous state, and it is now applied to solids. Neglecting the external pressure, the co-volumes of several elements in the solid state have been calculated, and the values obtained are considerably smaller than the co-volumes of compounds. For the metals, the value of the co-volume ($v - b$) increases with the volume (v), but the non-metals have to be arranged in families to show such a regularity. The value of the internal pressure, as calculated by Richards (*Abstr.*, 1902, ii, 304), is almost exactly three times as much as that calculated from van der Waals' equation, and it is concluded that of the heat introduced into a solid metal one-third is used in doing work against the internal pressure, and the remaining two-thirds are employed in increasing the potential energy of the molecules. It is shown that the coefficient of expansion of the co-volume by heat is $1/273$.

The hardness and elasticity of the elements have also been compared. Too much dependence must not be placed on the hardness, as this is

very much modified by the presence of impurities, but it is found that the modulus of elasticity and the internal pressure run parallel.

The product of internal molecular heat of vaporisation and coefficient of expansion is equal to the gas constant, and consequently this internal molecular heat of vaporisation is for all elements inversely proportional to the coefficient of expansion.

There exists a proportionality between the compressibility of metals and their co-volumes, and the length of the path traversed by the atom as calculated from van der Waals' equation ($\sqrt[3]{v} - \sqrt[3]{b}$) is directly proportional to that calculated by Meyer (*Ann. Physik*, 1897, 61, 225) from the diffusion of other metals in mercury.

The author concludes that van der Waals' equation of condition applies to the three states of aggregation. J. McC.

Finding of Transition Points with a Self-registering Dilatograph. R. VON SAHMEN and GUSTAV TAMMANN (*Ann. Physik*, 1903, [iv], 10, 879—889).—The principle underlying the apparatus described as a dilatograph is the comparison of the linear expansions of two substances; one of these is a substance whose expansion with rise of temperature is known and regular, the other is the substance to be investigated. Silver, in the form of a tube, is taken as the standard of comparison, and the other substance, in the form of a rod or prism, occupies the centre of this tube. The movements of the ends of the tube and rod, resulting from gradual rise of temperature, are magnified by levers, and are traced side by side on the surface of a revolving drum. Any discontinuity in the curve tracing the movement of the rod betrays a transition point, and by comparison with the curve for the silver tube the transition temperature can be determined.

With this apparatus, it is found that sodium pyrophosphate has two transition points at 390° and 520°; with rising temperature, the transitions are accompanied by a contraction and expansion respectively. Other transition points were discovered: potassium carbonate at 400°; sodium carbonate at 300° and 450°; sodium sulphate at 200°; thallium sulphate at 400° and 460°; fluorspar at 300°. J. C. P.

Phase Rule. RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1903, 43, 93—103).—A theoretical paper, unsuitable for abstraction. The case is specially considered in which there are two solid phases differing only in the sign of their rotation. J. C. P.

Conception of Independent Components. RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1903, 43, 89—92).—The author considers that the current definitions of components (as the word is used in connection with the phase rule) are either erroneous or inadequate. A fresh definition is suggested. J. C. P.

Proof of Gibbs' Phase Rule. WALTHER NERNST (*Zeit. physikal. Chem.*, 1903, 43, 113—114).—A reply to some of Wegscheider's criticisms of current definitions of components (see preceding abstract). J. C. P.

Velocity of Formation of the Acetates of some Closed-chain Alcohols. K. PANOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 93—100).—The author has determined the velocity of acetylation of various alcohols by heating together molecular proportions of the alcohol and acetic anhydride at 100° in presence of 15 volumes of benzene. The values obtained for k are as follows:

Phenol, 0.0242; *o*-cresol, 0.00721; *m*-cresol, 0.0277; *p*-cresol, 0.0234; thymol, 0.0051; 1:3-methylcyclohexanol, 0.0143; menthol, 0.0052; terpineol gives values which decrease rapidly as the esterification proceeds; *d*-borneol, 0.0112; *l*-borneol, 0.0111; isoborneol, 0.00773.

These results show that closed-chain alcohols possess greater esterification constants than open-chain alcohols having the same number of carbon atoms. Further, if a side-chain enters the molecule of a closed-chain alcohol in the ortho-position relatively to the hydroxyl residue, the velocity of esterification is lowered, whilst in the other positions, at any rate in the benzene nucleus, the introduction of a side-chain may produce an increase in the esterification constant. T. H. P.

Change of the Velocity of Amidification of Acids with Reference to their Structure. NICOLAI A. MENSCHUTKIN, J. KRIEGER, and M. DITRICH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 103—113).—The authors have determined the velocities with which the ammonium and dimethylamine salts of the following acids are converted into the corresponding amides or substituted amides; formic, acetic, propionic, butyric, isobutyric, isovaleric, methylethylacetic, hexoic, benzoic, *o*-, *m*-, and *p*-toluic, mesitylenic, phenylacetic, phenylpropionic, cinnamic, and hexahydrobenzoic. From the results obtained, the following conclusions are drawn: with the saturated acids, the velocity of formation of the amides is greatest for the acids having an unbranched chain of carbon atoms; the speed is diminished by the introduction of a side-chain, the diminution being more marked the greater the number of such side-chains and the nearer they are to the carboxyl group. For aromatic acids, the carboxyl-residue of which is contiguous to a carbon atom of the benzene nucleus, the velocity of amidification is less than is generally the case for tertiary acids. The influence of a side-chain in these acids is a very important one; if, in the ortho-position, it causes a diminution in the velocity of amidification, whilst in the meta- or para-position it may have an accelerating effect. Aromatic acids having the carboxyl group in the side-chain behave in an analogous manner to the saturated acids, the primary acids having a high, and the secondary acids a low, rate of amidification. This influence of the side-chain on the velocity of a reaction has been already observed in the formation of esters from alcohols and in some other reactions. T. H. P.

Relation to Temperature of the Rate of Crystallisation in the Case of Substances which have only a Low Rate of Crystallisation. W. BORODOWSKY (*Zeit. physikal. Chem.*, 1903, 43, 75—88; and *J. Russ. Phys. Chem. Soc.*, 1903, 35, 128—146).—When

rate of crystallisation is plotted against temperature, it is found that for substances with a small velocity of crystallisation a curve is obtained with a well-marked maximum; cases of this were cited by Bogojawlensky (*Abstr.*, 1899, ii, 206). The author has studied the extent to which this maximum is displaced by varying the bore of the tube in which crystallisation takes place, the substances employed being β -hydroxy- β -*p*-nitrophenylethyl methyl ketone, salipyrine, peucedanin, formanilide, and orthophosphoric acid. For these substances, the maximum lies generally $15\text{--}20^\circ$ below the melting point, provided the tubes used are of nearly equal bore, and it is found that from the melting point to the maximum point the rate of crystallisation increases almost proportionally to the extent of the supercooling. The influence of impurities is most marked in this ascending branch of the curve. Before the maximum point is reached, a portion of the supercooled liquid remains as such between the crystals, whilst after the maximum point has been passed the solidification is complete, or practically so. When the bore of the crystallisation tube is diminished, the influence of the heat of crystallisation on the rate of crystallisation is smaller, and accordingly the maximum is displaced towards higher temperatures. This observation, along with experiments in which a metal wire was introduced into the crystallisation tube to carry off the heat of crystallisation, led to the conclusion that if the crystallisation took place isothermally the rate of crystallisation would diminish with falling temperature from the melting point downwards.

Two modifications of salipyrine exist, characterised by different melting points, 91.8° and 86.3° , and by different rates of crystallisation. Orthophosphoric acid is also dimorphous and exists (1) as transparent crystals, m. p. 36.6° ; (2) as milk-white crystals, m. p. 41° ; at low temperatures, the latter modification passes very readily into the former.

J. C. P.

Properties of Sodium Sulphate Solution. CHARLES MARIE and R. MARQUIS (*Compt. rend.*, 1903, 136, 684—685).—The solubility of sodium chloride in a solution containing 7.45 grams of anhydrous sodium sulphate per 100 grams of solution has been determined at temperatures varying from 14.8° up to 34.28° . This temperature interval includes the transition temperature (32.38°) of crystallised sodium sulphate and the transition temperature (16°) in presence of excess of sodium chloride.

When the results are plotted graphically, a perfectly continuous curve is obtained showing no change of direction at these transition temperatures. This shows that the properties of the solution undergo no sudden change within this temperature interval, and the authors conclude that there is no reason to believe that in the solution the salt exists combined with those molecules of water which are an integral part of the crystallised molecule.

J. McC.

Influence of Inorganic Salts on Solubility. WILHELM BILTZ (*Zeit. physikal. Chem.*, 1903, 43, 41—48).—On the lines of Rothmund's work (*Abstr.*, 1900, ii, 467. Compare also Gordon, *Abstr.*, 1896, ii, 154; Roth, *Abstr.*, 1898, ii, 18; Euler, *Abstr.*, 1900, ii, 196).

Theoretically, the solubility of an indifferent substance, such as phenylthiocarbamide, should be unaffected by the presence of inorganic salts, but actual investigation shows that this is not so. Of sodium perchlorate, chlorate, and chloride, the first-mentioned has the least effect on the solubility of phenylthiocarbamide; the third exerts the most marked influence, for the solubility (in millimols. per litre) of phenylthiocarbamide is 13.9 in pure water, and only 10 in *N*/1-sodium chloride. Thus, the smaller the anion, the greater, *ceteris paribus*, is the influence of the salt on the solubility; this rule holds also for the relative effects of (1) potassium chlorate and chloride; (2) the nitrates and nitrites of sodium and potassium. It is to be noted, however, that phenylthiocarbamide is more soluble in dilute solutions of sodium and potassium nitrites than in pure water, which peculiarity is possibly due to a chemical action of nitrous acid on phenylthiocarbamide.

When the alkali metals are ranged in a series according to the influence of their nitrates on the solubility of phenylthiocarbamide, the order is not Li, Na, NH_4 , K, Rb, Cs, as might be expected (See Biltz, *Abstr.*, 1902, ii, 310), but Na, K, Li, Rb, NH_4 , Cs. It is remarkable that the solubility of phenylthiocarbamide is increased not only by ammonium nitrate (see Rothmund, *loc. cit.*), but also by caesium and rubidium nitrates.

Of the salts of the halogen acids, the chlorides have the greatest effect in diminishing the solubility of phenylthiocarbamide, whilst bromides are next in order. Potassium and sodium iodides increase the solubility somewhat.

J. C. P.

Working with Liquefied Gases. ALFRED STOCK and BERTHOLD HOFFMANN (*Ber.*, 1903, 36, 895—900).—The tubes are best made of ordinary soft glass or so-called "doubly cooled," readily fusible glass. If free from flaws, a tube of 10 mm. inner diameter and 12.4 mm. outer diameter will withstand the pressure of liquefied ammonia at 100° (about 60 atmospheres). If the inner diameter is increased to 20 mm., the walls of the tube should be correspondingly increased to 2 mm. It is not advisable to increase the diameter of the tube beyond 20 mm. unless the tubes are not to be heated.

The filter tube, previously described (*Ber.*, 1901, 34, 3042), has been modified by making the bulb in which the filter is placed somewhat smaller, and by lengthening the contraction on either side of this bulb.

A tube is also described by means of which continuous extraction or washing can be accomplished.

J. J. S.

Distribution of Hydrogen Sulphide to Laboratory Classes. CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1903, 25, 231—236).—A convenient form of generator, and of distribution of the gas is described. For details, the original must be consulted. A. McK

Inorganic Chemistry.

Solidification of Fluorine, and the Combination of Solid Fluorine and Liquid Hydrogen at -252.5° . HENRI MOISSAN and JAMES DEWAR (*Compt. rend.*, 1903, 136, 641—643).—It has previously been shown that fluorine liquefies at -187° (Abstr., 1897, ii, 446). A tube containing fluorine shows no condensation when immersed in liquid oxygen, but on slowly lowering it into liquid hydrogen a yellow liquid is produced which soon sets to a solid. After immersion for a sufficient time to allow the solid fluorine to assume the temperature (-252.5°) of the boiling hydrogen, it becomes perfectly white. By immersing a tube of fluorine in liquid nitrogen, partial liquefaction takes place, and by cooling to -210° by reducing the pressure over the liquid nitrogen the fluorine did not solidify. A tube containing fluorine was placed within one full of oxygen, and the two gases solidified in liquid hydrogen. On withdrawing, and so allowing the temperature to rise, the oxygen melted first, and the authors estimate the melting point of fluorine to be -223° (oxygen melts at -225°). The ratio of melting point to boiling point is a little smaller than in the case of chlorine and bromine.

A thin glass tube, in which 40 c.c. of gaseous fluorine had been solidified, was immersed in 100 c.c. of liquid hydrogen, and after the temperature of the fluorine was in equilibrium with that of the hydrogen the tube was broken. A violent explosion occurred and sufficient heat was developed to raise the materials to incandescence and cause the hydrogen to inflame. The violence of the explosion was sufficient to reduce to powder the double-walled glass vessel containing the liquid hydrogen.

J. McC.

Probable Atomic Weight of Tellurium, and Atomic Weight Calculations in General. PAUL KÖTHNER (*Zeit. anorg. Chem.*, 1903, 34, 403—409).—It is shown that Seubert's calculation (*ibid.*, 1903, 33, 247) of the atomic weight of tellurium, on the basis $H=1$, is too low. Seubert has calculated from the rounded off number 127.6 on the basis $O=16$, and his rounded off number is 126.6, whereas when the calculation is made with the more exact number 127.638, and then rounded off, a value more nearly 126.7 is obtained. The principle adopted by Seubert is apt to give rise to errors of considerable magnitude.

The author discusses the various determinations of the atomic weight of tellurium which have been made and concludes that the most probable value is 126.71 ($H=1$).

J. McC.

Absorption of Ammonia by Sea-water. J. THOULET (*Compt. rend.*, 1903, 136, 477—478).—Distilled water and sea-water become richer in free ammonia and slightly richer in albuminoid ammonia by

filtration through paper. The increase is proportional to the number of filtrations and does not depend on the nature of the filter; the ammonia of the air appears to be fixed by the material of the filter. Distilled water and sea-water directly absorb the ammonia diffused in the air, but the coefficient of absorption is greater in the case of sea-water. The first portions of the water which pass through the filter deprive the paper of all adherent ammonia.

W. D. H.

Preparation of Nitrous Oxide. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 59—61).—The methods usually employed for preparing nitrous oxide from ammonium nitrate yield a gas containing appreciable quantities of nitrogen, nitric oxide, and some other impurities. In order to obtain a continuous stream of the pure dry gas, the author gives the following method: a tube of difficultly fusible glass, sealed at one end, is filled with a mixture of 3 parts of dry sea-sand and 2 parts of ammonium nitrate dried at 105° , which is kept in position by an asbestos plug; the end of the tube is closed by a cork through which passes a delivery tube with tap. A small aluminium box, fitted with a thermometer and serving as an air-bath, is arranged to slide along the tube. The best temperature to employ is 260 — 285° , and the back end of the tube is first heated; when all the air has been expelled from the tube, the gas is passed, first through aqueous ferrous sulphate or alkaline sodium sulphide solution, and then through an emulsion of dry ferrous sulphate in concentrated sulphuric acid; it is then pure and dry.

T. H. P.

Direct Synthesis of Nitrogen Trioxide. DEMETRIO HELBIG (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 166—173. Compare Abstr., 1902, ii, 654).—The author finds that the flocculent, green substance obtained when a series of electrical discharges is passed through liquid air (*loc. cit.*) consists of nitrogen trioxide. In the present paper, he describes in detail the best method for obtaining the trioxide, which has not previously been prepared in a pure state. When suspended in the excess of liquid air, nitrogen trioxide bears a strong resemblance to precipitated chromic hydroxide, but when the air has been removed by evaporation under reduced pressure it forms a slightly blue, amorphous powder. It melts at -111° , and at the same time assumes a deep azure colour, which persists after the liquid has been resolidified by immersion in liquid air. The fused anhydride decomposes, yielding nitric oxide, which is also evolved when the liquid is placed in a vacuum. Gasometric analysis of the trioxide gives numbers agreeing with the formula.

T. H. P.

New Synthesis of Nitrogen Pentoxide. DEMETRIO HELBIG (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 211—214).—Nitrogen pentoxide is obtained by the action of ozone on nitrogen tetroxide. The best method for carrying out this synthesis is described in detail.

T. H. P.

Emanation of Phosphorus. GERHARD C. SCHMIDT (*Ann. Physik*, 1903, [iv], 10, 704—729).—Phosphorus which is undergoing slow oxidation imparts conductivity to the air, as may be shown by placing a piece near two metallic plates, one of which is charged and the other connected with an electrometer. The fog of particles emanating from the phosphorus changes its normal direction under the influence of the electric force, and is attracted to the nearer of the two plates, whether the charge on the latter is positive or negative. The phenomenon is probably the same as the attraction of small bits of paper by a charged glass rod, and this view is supported by the observation that the current between the two plates above referred to increases pretty regularly with their potential difference, and does not reach a "saturation" value, as in the case of air ionised by the action of Röntgen or uranium rays.

Examination of water that has been exposed in the neighbourhood of slowly oxidising phosphorus shows the absence of nitrate and nitrite, and the presence of phosphoric and phosphorous or hypophosphorous acids, and comparative experiments in moist and dry air prove that the acids, not the oxides, of phosphorus are responsible for the conductivity imparted to air.

The behaviour of ammonium chloride, sodium, and sulphur was compared with that of phosphorus. When a fog of particles is produced by gently warming ammonium chloride, the air becomes a conductor. Sodium behaves exactly like phosphorus, whether undergoing slow or rapid oxidation; sulphur, on the other hand, which yields no solid oxidation products, has practically no effect on the conductivity of air.

Phosphorus undergoing slow oxidation has no action on a photographic plate wrapped in paper and protected by an aluminium envelope. The author considers that this, as well as the above-mentioned experiments, is quite opposed to any explanation of the phosphorus emanation based on the electron theory. J. C. P.

Heat of Transformation of White Phosphorus into Red Phosphorus. H. GIRAN (*Compt. rend.*, 1903, 136, 677—680).—It has generally been assumed that in the transformation of white phosphorus into the red variety 19·2 Cal. are developed. By applying Clapeyron's formula for the vapour tensions of the two varieties, the author shows that the heat change is probably about 4 Cal., that is, of the same order as that developed by the passage of crystallised arsenic into the amorphous form.

To ascertain experimentally the heat change, the heat of combustion in oxygen has been determined in a Mahler calorimeter. The violet crystallised phosphorus obtained by crystallisation from fused lead was also examined. From the results obtained, it is deduced that $P(\text{white}) = P(\text{red}) + 3\cdot7 \text{ Cal.}$; $P(\text{red}) = P(\text{violet}) + 0\cdot7 \text{ Cal.}$; and therefore $P(\text{white}) = P(\text{violet}) + 4\cdot4 \text{ Cal.}$

The heats developed by the action of bromine on the various varieties of phosphorus lead to the results: $P(\text{white}) = P(\text{red}) + 4\cdot22 \text{ Cal.}$; $P(\text{red}) = P(\text{violet}) + 0\cdot23 \text{ Cal.}$; and $P(\text{white}) = P(\text{violet}) + 4\cdot45 \text{ Cal.}$

The heat of transformation of white into red phosphorus is therefore

about 4 Cal., whilst the heat of transformation of the red into the violet modification is about 0.5 Cal. The latter result is insufficient to definitely characterise the red and the violet as different modifications (compare Chapman, *Trans.*, 1899, 75, 734). J. McC.

Phosphorus. RUDOLF SCHENK (*Ber.*, 1903, 36, 979—995).—A bright red polymerisation product is produced on boiling a solution of white phosphorus in phosphorus tribromide for several hours (compare *Abstr.*, 1902, ii, 205). This insoluble red form carries down mechanically with it large quantities of the solvent, and similar precipitates are obtained containing other substances, such as phosphorus tri-iodide, originally dissolved in the tribromide. These are regarded as solid solutions of the foreign matter in red phosphorus, and their ready formation suggests that red phosphorus is amorphous.

The bright red form of phosphorus darkens on heating until its colour approaches that of ordinary commercial red phosphorus. It is non-poisonous, although chemically exceedingly active, as it precipitates copper from copper sulphate solution and reacts with alkalis more energetically than white phosphorus does. Alkalis, especially strong aqueous ammonia, cause an intense black coloration; this is a specific reaction of the finely divided red phosphorus, and is not shown by the commercial article. A black substance is also formed on boiling with aqueous piperidine solutions, the solution at the same time becoming bright red; the black substance then contains a large amount of piperidine. On decomposition with acids, a yellowish-red substance is formed, somewhat similar to the solid phosphorus hydride, which contains hydrogen and has the composition $P_6P_4H_2$.

Similar experiments with pure solid hydrogen phosphide, P_4H_2 , showed that it forms the same black substance with piperidine and alkalis, that obtained by the action of the latter having the formula $P_{10}H_4C_5H_{11}N$. These results suggest that the yellowish-red substance is a feebly acid hydrogen polyphosphide, that the black substances are alkali and piperidine salts of the acid respectively, and that the red solutions with piperidine are solutions of polyphosphides.

E. F. A.

Phosphorus Sesquisulphide. JULIUS MAI and F. SCHAEFFER (*Ber.*, 1903, 36, 870—877).—Owing to the very large use of the sulphide of phosphorus, P_4S_3 , in the manufacture of matches, and to the great importance that it should be free from phosphorus, especially yellow phosphorus, a careful investigation has been made of the conditions under which phosphorus is found in phosphorus sesquisulphide.

The crude commercial sulphide, which had been made by gradually heating red phosphorus with some excess of sulphur to a temperature of 330° in a current of carbon dioxide, was heated for 2—3 hours at 180° in a stream of dry carbon dioxide; the evolution of hydrogen phosphide was observed, and the formation of a crystalline sublimate; this was obtained in much larger quantity when the sulphide was heated at 340° . This sublimate was luminescent at 40° when

observed in the dark, and at that temperature evolved white vapour; it melted at $155-164^{\circ}$, was readily soluble in carbon disulphide, and is undoubtedly phosphorus sesquisulphide free from phosphorus. In this state, it melts to an amber-yellow liquid, and not red as is usually stated. A further series of experiments were made with phosphorus sesquisulphide, which had been obtained from the crude product by repeated crystallisation from a mixture of carbon disulphide and petroleum. When heated at $40-50^{\circ}$, it luminesces strongly, emits a white vapour, and becomes slowly oxidised. When boiled with water (Mitscherlich's test for free phosphorus), luminescence was seen as long as the water was boiled, but ceased as soon as the boiling was stopped. After prolonged distillation with steam, a minute quantity of solid distillate was obtained which consisted mainly of phosphorus sesquisulphide mixed with a small quantity of oxidised substances; the condensed steam contained hydrogen sulphide.

On heating the sesquisulphide in a slow current of carbon dioxide at 380° , when the substance gently boiled for several hours, a red sublimate was rapidly formed just above the liquid, and at the same time a very small distillate was obtained; the red sublimate appeared to be mainly red phosphorus. That portion of the distillate which was collected as oily drops in the condensing tube was carefully investigated; after five hours, it amounted to little more than 0.1 gram, which consisted of the sesquisulphide mixed with under 10 per cent. of yellow phosphorus.

It would therefore appear that the use of too high a temperature in the preparation of phosphorus sesquisulphide would lead to the separation of phosphorus; in a specimen of the commercial product in the preparation of which a temperature of 340° had been attained, yellow phosphorus was undoubtedly found. When too low a temperature has been used, the sesquisulphide cannot be powdered, a process which is essential in the manufacture of matches.

K. J. P. O.

Precipitation of Colloidal Arsenious Sulphide Solutions. FRIEDRICH W. KÜSTER and GEORG DAHMER (*Zeit. anorg. Chem.*, 1903, 34, 410—412).—Hydrogen sulphide produces arsenious sulphide with an aqueous solution of arsenious oxide, but the sulphide formed remains dissolved colloiddally (this vol., ii, 74). Vanino (*Abstr.*, 1902, ii, 249) has remarked that heavy spar quickly precipitates colloidal solutions. The pseudo-solution of arsenious sulphide is only slowly precipitated by barium sulphate; vigorous shaking is required, and precipitated barium sulphate causes the effect better than the powdered mineral. Furthermore, a large quantity of the solid is necessary.

The precipitation is also brought about by charcoal, copper oxide, glass powder, and best of all by powdered Iceland spar. J. McC.

Silicic Acid. I. EDUARD JORDIS (*Zeit. anorg. Chem.*, 1903, 34, 455—460).—The author has endeavoured to find a well-defined substance to serve as starting point in the investigation of silicic acid and the silicates.

Pure silicic acid can be obtained from "water glass" by decomposing a concentrated solution with concentrated hydrochloric acid (10—16*N*). The granular silicic acid which is precipitated is washed, then treated with potassium permanganate and hydrochloric acid to destroy organic matter. The manganese is completely removed by washing with sulphuric acid, which, in turn, is thoroughly washed out with water. The product is dried in the air-bath, then dissolved in the calculated quantity of sodium hydroxide solution ($\text{Na}_2\text{O} : 2\text{SiO}_2$), and the solution diluted so that it contains 3 to 5 per cent. of silicon dioxide. The solution is decomposed by the calculated quantity of hydrochloric acid in about the same volume of water. The gelatinous silicic acid is washed in running water and digested with dilute hydrochloric acid to remove the last trace of alkali. After finally washing with water, the gelatinous mass is allowed to drain and then contains about 95 per cent. of water. The silicic acid thus obtained is very sparingly soluble in water, but no dependence is to be placed on the solubility determined, as this was carried out in a glass vessel, and even a minute quantity of alkali conditions the solubility of a considerable quantity of silicic acid. J. McC.

Direct Combination of Chlorine and Carbon. WERNER VON BOLTON (*Zeit. Elektrochem.*, 1903, 9, 209—210).—The author has prepared hexachlorobenzene by the method described previously (*Abstr.*, 1902, ii, 393) in quantity sufficient for an analysis. The results show that the substance really is hexachlorobenzene. T. E.

Study of the Interaction of Carbon Dioxide and Potassium Hydride. HENRI MOISSAN (*Compt. rend.*, 1903, 136, 723—727).—It was recently shown that potassium hydride and carbon dioxide unite to form potassium formate (*Abstr.*, 1902, i, 255); a careful study proves that this reaction only takes place in the presence of a trace of water. The hydride was prepared from potassium free from hydroxide and hydrogen which had been dried first by fused potassium hydroxide and then by bright sodium wire; the carbon dioxide was dried by fused potassium carbonate and sodium, and in some cases by passage through a vessel immersed in liquid oxygen. Under these conditions, no reaction between the hydride and the carbon dioxide took place at the ordinary temperature, but when the temperature was raised to 54°, combination immediately occurred, a small flame being seen to play over the surface of the potassium hydride. In these experiments, great difficulty was met with in drying the apparatus; lead tubes were used instead of indiarubber to connect the different parts of the apparatus, through which was passed a current of dry gas for a long period; in some cases, the glass parts were exhausted and heated at 130°. The nature of the glass appears to be without influence on the interaction of the carbon dioxide and potassium hydride; in this respect, it offers a contrast to the combination of hydrogen and oxygen, which only refuse to interact in Jena glass (*Brereton Baker, Trans.*, 1902, 81, 400).

In order to ascertain what quantity of water is necessary for the

combination of the hydride and carbon dioxide at the ordinary temperature, the carbon dioxide was passed over ice at -20° before it came in contact with the dry hydride; but it was found that the dry glass and lead tubes absorbed the trace of water vapour mixed with the carbon dioxide, and consequently the gas had to be passed for a long time before it arrived at the hydride in a moist condition. In later experiments, a small sealed bulb, which contained mercury and from $1/5$ to 3 mg. of water, was placed in the tube in which the hydride was about to be prepared; the hydride being produced, the tube, which was then filled with dry carbon dioxide, was sealed, and after being cooled to various temperatures the small sealed bulb was broken. Neither at -182.5° (liquid oxygen) nor at -90° did any reaction take place, but at -85° , when the solid carbon dioxide began rapidly to volatilise, interaction with development of heat occurred. If the bulb containing the water was not broken, the hydride and the carbon dioxide did not combine. It is therefore demonstrated that the quantity of water corresponding with the vapour tension of water at -85° is sufficient to bring about the reaction. This quantity is less than 0.25 mg.

The hydrides of sodium, rubidium, and caesium do not combine with dry carbon dioxide, but in the presence of a trace of water immediately yield formates.

Experiments have shown that traces of hydrogen chloride or ammonia are not able to bring about the combination of metallic hydrides and carbonic dioxide in the same manner as does water.

K. J. P. O.

Action of Hydrogen Peroxide on Acid Carbonates. P. KASANEZKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 57—59. Compare Abstr., 1902, ii, 317, and 500).—When potassium hydrogen carbonate is treated with a large excess of hydrogen peroxide solution and the resulting liquid mixed with 4 to 5 times its volume of alcohol, the compound $K_2CO_3 \cdot 2\frac{1}{2}H_2O$, previously obtained by the author (*loc. cit.*), is precipitated. Similarly, sodium hydrogen carbonate yields the compounds $Na_2CO_3 \cdot 1\frac{1}{2}H_2O$ and $Na_2CO_3 \cdot \frac{1}{2}H_2O_2 \cdot H_2O$, already obtained by Tanatar (Abstr., 1899, ii, 482) from sodium carbonate. The formation of these compounds is accompanied by an evolution of carbon dioxide similar to the liberation of boric acid during the interaction of hydrogen peroxide and borax.

T. H. P.

Revision of the Atomic Weight of Cæsium. THEODORE W. RICHARDS and EBENEZER H. ARCHIBALD (*Zeit. anorg. Chem.*, 1903, 34, 353—382; and *Proc. Amer. Acad.*, 1903, 38, 443).—To purify the cæsium salt, it was converted into the dichloriodide, $CsCl_2I$, which was repeatedly recrystallised, then converted into the chloride by heating at 90 — 100° . The chloride was then dissolved in as little water as possible and either precipitated with alcohol or with hydrogen chloride. To completely free the salt from moisture, it was ignited in a current of pure nitrogen and transferred to a weighing bottle without being brought into contact with the air. Twenty-five analyses of cæsium chloride were made; in 13, the weight of cæsium chloride was compared with silver chloride and in 12 with silver. The mean value

obtained for the atomic weight of caesium is 132·878, with a probable error of $\pm 0\cdot0007$ ($\text{Ag} = 107\cdot930$, $\text{Cl} = 35\cdot455$). In order to verify the exactitude of the method, a similar determination was made with potassium chloride; the atomic weight found for potassium was almost identical with that determined by Stas.

By experiments with potassium nitrate, it was proved that the method of heating the nitrate with silica and determining the loss of weight (N_2O_5) gives accurate results. Four results obtained with pure caesium nitrate, produced from pure caesium dichloriodide, lead to the atomic weight 132·879 for caesium ($\text{O} = 16\cdot000$, $\text{N} = 14\cdot040$). The silica used was a carefully purified and ground sand. The heating was carried out in a platinum crucible protected from the gases of the flame. Caesium tribromide was prepared from the nitrate by the action of hydrobromic acid and bromine. By heating at 80° , it was converted into the bromide, which was ignited in a current of nitrogen and analysed. Three analyses in which the ratio of caesium bromide to silver bromide was determined gave 132·880 as atomic weight of caesium, and three in which the ratio of caesium bromide to silver was determined gave 132·881 ($\text{Br} = 79\cdot955$).

The mean result for the atomic weight of caesium is 132·879.

Incidentally, the following constants have been determined: sp. gr. of caesium chloride, bromide, and nitrate, 3·972, 4·380, and 3·687 at $20^\circ/4^\circ$ respectively; melting point of caesium nitrate, 414° .

During the course of the investigation, no indication was obtained of the existence of an analogous metal of higher atomic weight.

J. McC.

Iodides of Caesium. H. W. FOOTE (*Amer. Chem. J.*, 1903, 29, 203—212).—The periodides of caesium, CsI_3 and CsI_5 , have been described by Wells (Abstr., 1892, 773), and Wells and Wheeler (Abstr., 1893, ii, 67). It is shown by means of solubility determinations chiefly that these two compounds are the only periodides of caesium existing between -4° and 73° . The results obtained are found in all cases to agree with the theoretical conclusions deduced from the phase rule.

E. G.

Preparation and Properties of Rubidium and Caesium Hydrides. HENRI MOISSAN (*Compt. rend.*, 1903, 136, 587—591).—These hydrides are prepared by the same method as that employed in the preparation of potassium hydride (Abstr., 1902, ii, 136), namely, by heating the metal at about 300° in a current of hydrogen. Rubidium hydride, RbH , forms colourless, prismatic needles of sp. gr. about 2, whilst caesium hydride, CsH , is obtained in colourless, flattened, lustrous crystals and has a sp. gr. 2·7. In a vacuum at a temperature below 300° , both hydrides dissociate into hydrogen and metal. In fluorine, chlorine, bromine, or oxygen at the ordinary temperature, both hydrides are attacked with incandescence. With iodine, it is necessary to heat the mixture to start the reaction. Both hydrides are rapidly decomposed by fused sulphur. When heated in a current of nitrogen, a mixture of nitride and amide is formed. With phosphorus, a phosphide is formed, and at a higher temperature arsenic

also effects the decomposition of the hydrides. Carbon, boron, and silicon have no action at temperatures up to 300° . The decomposition with water into hydrogen and metal hydroxide takes place quickly at the ordinary temperature. Carbon dioxide has no effect at the ordinary temperature, but when the hydride is gently heated in a current of this gas, a formate is produced. In a rapid current of sulphur dioxide, a mixture of sulphide and sulphate is formed, but under diminished pressure a hyposulphite is produced ($2\text{RbH} + 2\text{SO}_2 = \text{Rb}_2\text{S}_2\text{O}_4 + \text{H}_2$). With hydrogen sulphide or hydrogen chloride, hydrogen is evolved and the metallic sulphide or chloride formed. At the ordinary temperature, ammonia produces the amide with evolution of hydrogen ($\text{RbH} + \text{NH}_3 = \text{RbNH}_2 + \text{H}_2$).

J. McC.

Collargol. MAURICE HANRIOT (*Compt. rend.*, 1903, 136, 680—682).—Collargol is a therapeutic product containing 87.3 per cent. of silver, besides proteid matter, a small quantity of ammonia, and a trace of nitric acid. It dissolves in water giving a reddish-brown solution, which closely resembles the colloidal solutions of silver described by Carey Lea. Addition of silver nitrate to the solution causes complete precipitation of the silver, both of the collargol and of the salt added. The precipitate is not metallic silver; it is soluble in solutions of nitric acid or of potassium cyanide, and the red colour again develops on the addition of ammonia. With copper sulphate or barium nitrate, a similar precipitation takes place, and the precipitates contain copper or barium respectively.

These results indicate that collargol is a salt capable of entering into reaction with other salts. By the action of dilute acetic acid on a solution of collargol, a black precipitate is obtained which behaves like an acid. It is insoluble in water, but soluble, with a reddish-brown colour, in solutions of ammonia, alkali hydroxides, or alkali carbonates. This *collargolic acid* is, therefore, a stronger acid than carbonic acid; the original collargol is the ammonium salt, and is hydrolysed by boiling with water. On electrolysing a solution of collargol, a black deposit of collargolic acid is obtained on the anode.

J. McC.

Hydraulic or so-called Estrich Gypsum. JACOBUS H. VAN'T HOFF and G. JUST (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 249—258).—Estrich gypsum is obtained by igniting natural gypsum at a temperature higher than 120 — 130° . It is anhydrous, and, under the influence of water, it hardens much more slowly than plaster of Paris obtained by burning gypsum at 120 — 130° , which is the semihydrate, $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. Estrich gypsum consists of calcium sulphate containing a very small amount of lime. A microscopic examination has proved that it consists of needle-shaped crystals, pseudomorphous with the semihydrate. The influence of the temperature of ignition on the hardening of the product was determined by noting the change of volume when in contact with water and by weighing the water taken up. The dilatometric observation with the semihydrate shows that at first a contraction takes place which is followed by an expansion, but the whole effect is one of contraction, and this apparent abnormality is

explained by the solubility relationships of the semihydrate and the dihydrate. The semihydrate only gives up water with an appreciable velocity above 190° . Specimens of the semihydrate were heated for 10 hours at 200° , 300° , and 400° respectively, and the products examined at 25° in a dilatometer with a saturated solution of calcium sulphate. Contraction took place regularly, more quickly with the product obtained at 200° than with those formed at the higher temperatures. The results, as also those found from weighing the water absorbed, show that Estrich gypsum which is not formed at too high a temperature, can by ignition be converted into a form which does not harden in contact with water.

During the ignition to calcium sulphate, which does not harden, the crystalline structure is destroyed.

Well-crystallised semihydrate, crystalline alabaster, and gypsum obtained from plaster of Paris were heated at a dull red heat for 5 minutes, then placed in contact with water. In the course of 3 days, the first had become quite hard, and, after 12 days gypsum crystals were plentiful in the second specimen, whilst the third only showed a few single gypsum crystals.

J. McC.

Sub-salts of Barium. ANTOINE GUNTZ (*Compt. rend.*, 1903, 136, 749—751).—Although sodium sets free calcium from calcium chloride, the chlorides of barium and strontium are not thus decomposed (Caron, *Compt. rend.*, 1859, 48, 440). With the object of learning the cause of this difference, barium chloride, bromide, iodide, and fluoride have been heated at high temperatures with sodium in mol. proportions. In the case of barium iodide, no reaction occurred at 400° , but at 800° to 1000° a change had taken place, the contents of the crucible consisting of a crystalline mass covered with sodium. Similar results were found with the other salts; the crystalline solids were the double salts, BaI, NaI , BaBr, NaBr , BaCl, NaCl , and BaF, NaF . The latter had previously been prepared by Limb by the action of sodium or the double fluoride, BaF_2, NaF . With the exception of the fluoride, these salts decompose water easily; when heated under reduced pressure at 700° , sodium volatilises, leaving barium chloride. On treatment with mercury, barium amalgam is formed, and when heated in hydrogen or nitrogen the hydride and nitride are respectively produced.

These results probably account for the non-formation of barium in the electrolysis of the double chloride, $\text{BaCl}_2, \text{NaCl}$; the sodium chloride is first decomposed, and the sodium then reacts with the barium chloride forming the double salt, BaCl, NaCl ; at the anode, this salt is again converted into barium chloride and sodium chloride, a fact which accounts for the cessation of the evolution of chlorine in the later stages of electrolysis.

K. J. P. O.

Crystalline Form of Radium Bromide. FRIEDRICH RINNE (*Centr. Min.*, 1903, 134—141).—Crystals of radium bromide are monoclinic [$a : b : c = 1.4485 : 1 : 1.1749$; $\beta = 65^{\circ}24'$] and isomorphous with barium bromide ($\text{BaBr}_2, 2\text{H}_2\text{O}$).

L. J. S.

Magnesium Carbonate and some of the Double Compounds which it forms. GEORG VON KNORRE (*Zeit. anorg. Chem.*, 1903, 34, 260—285).—When crystallised magnesium carbonate ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is suspended in a saturated solution of potassium chloride through which carbon dioxide is passed, the double salt, $\text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$, is formed, from which potassium carbonate may easily be obtained. Rhombic crystals of magnesium carbonate trihydrate can be obtained by (1) leaving a solution of magnesium hydrogen carbonate exposed to the air, (2) the addition of a solution of an alkali hydrogen carbonate to one of a magnesium salt, (3) leaving the precipitate produced by the addition of sodium carbonate to a solution of a magnesium salt in contact with the liquid. The separation of the crystals is slow, and the temperature should not be allowed to fall below 15° or the unstable pentahydrate, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$, is deposited. The magnesium carbonate may be washed without undergoing decomposition. When finely divided, it readily loses some of its water of crystallisation in the air. When the salt effloresces, no carbon dioxide is lost. It has a sp. gr. 1.808 at 18° . Attempts to prepare the carbonate, $4\text{MgCO}_3 \cdot 15\text{H}_2\text{O}$, described by Kippenberg (*Abstr.*, 1894, ii, 281), led only to the formation of the trihydrate.

The double salt, $\text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$, can also be prepared by the action of excess of potassium hydrogen carbonate on magnesium chloride in aqueous solution; it is somewhat soluble in water, *per se*, but is quickly decomposed with precipitation of basic magnesium carbonate. It has a sp. gr. 1.984 at 18° .

The double salt, $\text{MgCO}_3 \cdot \text{K}_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, is produced by the action of potassium sesquicarbonate on magnesium salts or by digesting magnesium chloride with a large excess of a saturated solution of potassium carbonate (if magnesium sulphate is employed, the product always contains some sulphate as impurity). The salt is very easily decomposed by water.

With respect to the formation of double salts, sodium behaves quite differently from potassium. When precipitated magnesium carbonate is digested with excess of sodium sesquicarbonate solution, small crystals of the anhydrous double salt, $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3$, are deposited. The crystals are octahedral in appearance, and belong to the tetragonal system; they are isometric and show double refraction. It has not been possible to obtain the other sodium double salts described by Berzelius and by Deville.

The ammonium double salt, $\text{MgCO}_3 \cdot \text{NH}_4\text{HCO}_3 \cdot 4\text{H}_2\text{O}$, is formed by the action of excess of ammonium hydrogen carbonate on magnesium chloride. The salt is very easily decomposed by water. The double salt, $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, is much more stable. J. McC.

Incrustation on Bricks. RUDOLF WOY (*Zeit. öffentl. Chem.*, 1903, 9, 62—66).—Last spring, the bricks of a number of new buildings in Breslau became thickly coated with a white, crystalline deposit, as much as 10 grams being yielded by a single brick. This deposit was found to consist almost entirely of crystallised magnesium sulphate. At the same time, some of the bricks showed a green incrustation, consisting of salts of vanadic acid.

The bricks had stood for some time on a bed of slag and had evidently absorbed magnesium sulphate from it. Subsequent rain showers did not wash the magnesium sulphate out of the bricks again.
W. P. S.

A New Method for the Preparation of Plumbic Ammonium Chloride. ALPHONSE SEYEWETZ and P. TRAWITZ (*Compt. rend.*, 1903, 136, 686—687).—The process depends on the action of ammonium persulphate on lead chloride in presence of hydrochloric acid as represented by the equation: $(\text{NH}_4)_2\text{S}_2\text{O}_8 + 4\text{HCl} + \text{PbCl}_2 = \text{PbCl}_4 + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{SO}_4$. The lead chloride is shaken with four times the quantity of hydrochloric acid required by the equation and powdered ammonium persulphate is added in the cold in portions of 15—20 grams at a time, so that the temperature never rises above 30°. The plumbic ammonium chloride is precipitated at once and the yield is almost quantitative.

Lead sulphate may be used in place of the chloride, but in this case a larger excess of hydrochloric acid must be employed. J. McC.

Calcium-Lead Orthoplumbate. GEORG KASSNER (*Arch. Pharm.*, 1903, 241, 143—148).—When a mixture of calcium and lead oxides in the proportion $\text{CaO} : \text{PbO}$ is heated at 450—480° in a current of air freed from carbon dioxide, the product is not calcium metaplumbate, CaPbO_3 , but appears to be a mixture of uncombined lime with a mixed *calcium lead orthoplumbate*, CaPbPbO_4 . This has a red colour; hydrochloric acid acts on it with liberation of chlorine, whilst nitric and acetic acids cause a separation of lead dioxide; above 550°, it appears to decompose according to the equation $4\text{CaPbPbO}_4 = 2\text{Ca}_2\text{PbO}_4 + 6\text{PbO} + \text{O}_2$. C. F. B.

Cuprous Sulphate. ALEXANDRE JOANNIS (*Compt. rend.*, 1903, 136, 615—617).—The existence of a compound of cuprous sulphate and carbon monoxide has already been noticed (*Abstr.*, 1898, ii, 221). This has now been proved to have the formula $\text{Cu}_2\text{SO}_4 \cdot 2\text{CO} \cdot \text{H}_2\text{O}$. The white crystals of this substance effloresce readily. Under diminished pressure, either the solid or the solution undergoes decomposition into copper and cupric sulphate, which suggests that cuprous sulphate cannot exist except in combination with another molecule, such as carbon monoxide or phosphorus hydride. Solutions of cupric nitrate, formate, or acetate, in contact with metallic copper, absorb carbon monoxide and at the same time are decolorised. J. McC.

Aluminium Sulphates. OTTO SCHMATOLLA (*Zeit. angew. Chem.*, 1903, 16, 202—205).—The precipitation of aluminium sulphate by alkalis never leads to the formation of a hydroxide free from sulphate. The following basic sulphates have been obtained by the use of different precipitants. By the action of calcium carbonate on a cold solution of aluminium sulphate, the basic sulphate of the composition $\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ is formed; cold alkali hydroxides precipitate the basic sulphate $6\text{Al}_2\text{O}_3 \cdot \text{SO}_3$, cold ammoniacal solutions of ammonium salts, the sulphate $12\text{Al}_2\text{O}_3 \cdot \text{SO}_3$, boiling solutions of alkali hydroxides, the sulphate

$24\text{Al}_2\text{O}_3, 3\text{SO}_3$, and a strong solution of ammonia containing ammonium salts, the sulphate $48\text{Al}_2\text{O}_3, 3\text{SO}_3$. Aqueous ammonia, free from ammonium salts, converts the basic sulphate $48\text{Al}_2\text{O}_3, 3\text{SO}_3$ into pure aluminium hydroxide; the presence of ammonium sulphate therefore prevents the complete decomposition of the sulphate. That sulphuric acid does not merely adhere to the hydroxide is shown by the fact that heating to the very highest temperatures is required to completely drive off the sulphuric acid.

If calcium acetate is added to the acetic acid solution of the basic sulphate $12\text{Al}_2\text{O}_3, 3\text{SO}_3$, the precipitation of the sulphate by lead acetate is hindered; if the amount of calcium acetate bears to the amount of the aluminium hydroxide the proportion of 1 mol. acetate to 2 mols. hydroxide, no lead sulphate is precipitated.

When the sulphate $\text{Al}_2\text{O}_3, 3\text{SO}_3, 18\text{H}_2\text{O}$ is heated with concentrated sulphuric acid, a sparingly soluble sulphate, $\text{Al}_2\text{O}_3, 3\text{SO}_3, 6\text{H}_2\text{O}$, separates as a white, very light powder, which can be dried at 100° . Alcohol precipitates from aqueous solutions of aluminium sulphate, the sulphate $\text{Al}_2\text{O}_3, 3\text{SO}_3, 9\text{H}_2\text{O}$.
K. J. P. O.

Manganous Borate. HERMANN ENDEMANN and JOHN W. PAISLEY (*Zeit. angew. Chem.*, 1903, 16, 175—176).—Commercial manganous borate is of very varying composition. The precipitate obtained by mixing solutions of manganous chloride and borax in the proportion $\text{MnCl}_2 : \text{Na}_2\text{B}_4\text{O}_7$ is very unstable, losing boric acid and becoming oxidised when washed. A stable salt of constant composition can, however, be prepared by the action of an alkaline solution of borax ($4\text{NaOH} : \text{Na}_2\text{B}_4\text{O}_7$) on a solution of manganous chloride, the proportions of the reagents being $2\text{MnCl}_2 : 4\text{Na}_2\text{O} : 2\text{B}_2\text{O}_3$. The precipitate is collected by centrifugalising and washed twice with water; the oxide of manganese and boric acid, which is lost in washing, is estimated, and the requisite amount of boric acid added to the moist basic borate. When dried at the ordinary temperature, the solid has the composition given by the formula $\text{MnO}, 2\text{B}_2\text{O}_3, 5\text{H}_2\text{O}$, and when dried at 120° the composition $\text{MnO}, 2\text{B}_2\text{O}_3, 3\text{H}_2\text{O}$; the former contains 23.6 per cent. of manganous oxide, and the latter 27.2 per cent. This preparation makes a very good siccative for oils.
K. J. P. O.

Suggested Explanation of the Reduction of Permanganic Acid by Manganese Dioxide. J. C. OLSEN (*Amer. Chem. J.*, 1903, 29, 242—253).—The reduction of permanganic acid by manganese dioxide was observed by Morse, Hopkins, and Walker (*Abstr.*, 1896, ii, 475). It was suggested by Morse and Reese (*Abstr.*, 1898, ii, 588) that manganese dioxide may have a tendency to undergo polymerisation, and therefore may remove manganese dioxide from permanganic acid, oxygen being thus liberated. Morse and Byers (*Abstr.*, 1900, ii, 406) found that the action does not occur to any marked extent except in acid solution, and that the decomposition of the permanganate takes place much more rapidly in presence of nitric acid than in presence of an equivalent amount of sulphuric acid.

When both nitric and sulphuric acid are present in the same potassium permanganate solution, the influence of each cannot be calculated

from the amount of decomposition produced by each acid acting alone. If the acids are present in equal proportions, the amount of permanganic acid decomposed is much less than the mean of the quantities decomposed by each acid acting singly; even if the sulphuric acid forms but 5 per cent. of the total acid present, the decomposition is only 62 per cent. of that produced by nitric acid alone. If permanganic acid itself is used instead of the potassium salt, similar results are obtained; hence it is evident that the potassium is not the cause of this peculiarity of the decomposition.

[With F. S. WHITE.]—It was noticed that when manganese dioxide is precipitated by oxalic acid from a permanganate solution containing sulphuric acid, it retains part of the sulphuric acid with some persistence, whilst if it is precipitated from a solution containing nitric acid, the nitric acid can be easily removed by washing.

The phenomena observed in the reduction of permanganic acid by manganese dioxide can be explained by the weak basic properties of manganese dioxide and its tendency to unite with sulphuric acid rather than with nitric or permanganic acid. In order to test the accuracy of this hypothesis, the quantity of sulphuric acid retained by the precipitated manganese dioxide was estimated. The amount of available oxygen in the precipitate was also ascertained, since, if the permanganate solution were decomposed by the union of permanganic acid with the manganese dioxide, the precipitate would contain a larger proportion of oxygen than if it were pure manganese dioxide. The results show that the amount of sulphuric acid retained by the precipitate is inversely proportional to the excess of oxygen. It seems probable, therefore, that the manganese dioxide acts as a base and combines with sulphuric or permanganic acid. The permanganic permanganate readily decomposes with evolution of oxygen and formation of a polymerised manganese dioxide, which is a much less active compound than manganese dioxide itself.

E. G.

Crystalline Forms of Carbides and Silicides of Iron and Manganese. LEONARD J. SPENCER (*Min. Mag.*, 1903, 13, 296—302).

—Crystals of Spiegeleisen and ferro-manganese are of two kinds, with prism angles of $67\frac{1}{2}^\circ$ and about 60° respectively. Terminated crystals having the composition given under I and IV are orthorhombic and anorthic respectively. The other crystals, of which the composition and prism angle are given below, were without terminal faces:

	Fe.	Mn.	C.	Si.	Prism angle.
I.	34.80	56.80	3.90	3.31	66° about
II.	{ 59.35 60.00	{ 32.50 33.40	{ 6.08 5.85	{ 0.37 0.23	$67^\circ 32'$
III.	48.10	44.05	6.40	1.35	$67^\circ 33'$
IV.	67.40	20.10	1.63	10.50	60° about
V.	very little	much	much	very little	„
VI.	29.80	61.98	6.83	0.26	„
VII.	much	80	much	very little	„

L. J. S.

Theory of the Tempering of Steel. ANDRÉ LE CHATELIER (*Compt. rend.*, 1903, 136, 664—667).—The author has already shown that the carbon theory and the allotropic iron theory are incompatible with the existence of internal tensions in tempered steel. These tensions can only be due to changes of state accompanied by changes of volume, and the author believes that the change is from the magnetic to the non-magnetic condition. In these different conditions, the iron has different coefficients of thermal expansion, and on this basis a hypothesis has been constructed to account for the tempering of steel.
J. McC.

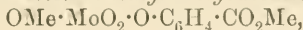
Hydrates of Molybdic Acid and some of their Compounds. ARTHUR ROSENHEIM and ALFRED BERTHEIM (*Zeit. anorg. Chem.*, 1903, 34, 427—447).—When equal volumes of a 15 per cent. solution of ammonium molybdate solution and nitric acid of sp. gr. 1.16 are mixed, *molybdic acid dihydrate*, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, separates. It forms canary-yellow prisms. The solubility in water has been determined at temperatures from 18° up to 79°. The solubility curve shows a marked change of direction at 70°, and by a dilatometric determination it was found that at 70° the dihydrate is transformed into the monohydrate. At 50°, there is also a change of direction of the solubility curve, and possibly below 18° another change of direction occurs. The solubility determined by saturating at a particular temperature is lower than that obtained by saturating at a higher temperature and then cooling in contact with solid. This anomalous behaviour cannot be satisfactorily explained, but it seems not to be due to the formation of a colloidal solution, because the apparently supersaturated solution diffuses quite readily. The conductivity of the solution and the catalysis of methyl acetate by it show that in solution the acid is highly dissociated.

Cryoscopic measurements indicate that in the solution an octomolybdic acid, $\text{H}_2\text{Mo}_8\text{O}_{23}$, is present and these are supported by the fact that on adding ammonium salts, ammonium octomolybdate, $(\text{NH}_4)_2\text{Mo}_8\text{O}_{25} \cdot 13\text{H}_2\text{O}$, separates.

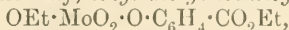
The *monohydrate*, $\text{MoO}_3 \cdot \text{H}_2\text{O}$, is always formed when the dihydrate is heated at 70°. It forms small, white needles which are very sparingly soluble in cold water, but more soluble in hot water; it has not been possible to effect the regeneration of the dihydrate.

The dihydrate is much more reactive than the ordinary molybdic anhydride, and with it the following compounds have been prepared. With oxalic acid, *oxalodimolybdic acid*, $\text{H}_2\text{C}_2\text{O}_4(\text{MoO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, as small, white crystals which become blue under the action of daylight. It is soluble in water, methyl alcohol, ethyl alcohol, and acetone, but insoluble in ether or benzene. With methyl alcohol, *methyl molybdate*, $\text{MoO}_2(\text{OMe})_2$, in the form of small, white crystals which become blue in the light. It is insoluble in methyl alcohol, sparingly soluble in ethyl alcohol, but very slightly soluble in water. Cryoscopic measurements indicate that dissociation takes place in aqueous solution. With acetylacetone, *molybdic acid acetylacetone*, $\text{C}_{10}\text{H}_{14}\text{O}_6\text{Mo}$ (possibly $\text{MoO}_2[\text{CH}(\text{COMe})_2]_2$), is formed in small, yellow crystals which are insoluble in water. With salicylaldehyde, *molybdic acid*

salicylaldehyde, $\text{MoO}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO})_2$, is produced, which crystallises from alcohol in long, yellow prisms. It is insoluble in cold water and is hydrolysed by hot water. *Methyl molybdosalicylate*,



is produced as a light yellow, crystalline powder by heating a suspension of dimethyl molybdate in methyl alcohol with methyl salicylate. In the same way, *ethyl molybdosalicylate*,



is formed as a whitish-yellow powder.

Acetic acid and boric acid exert scarcely any influence on the conductivity of molybdic acid solutions. Tartaric acid, malic acid, and mannitol greatly increase the conductivity, and this is attributed to the formation of a complex molecule. On account of hydrolysis of the complex molecule at high dilution, the increase of the conductivity diminishes somewhat with the dilution. Oxalic acid and iodic acid, which form complex molecules with molybdic acid, which can be isolated, diminish the conductivity, but this may be due to the complex ion having a smaller speed of migration. Phosphoric acid also increases the conductivity, the maximum being reached when phosphodecamolybdic acid is present.

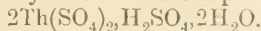
J. McC.

Condition in Solution of Salts of Hyperacids. L. PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 42—56).—From the results of conductivity experiments with solutions of peruranic and pervanadic acids, and measurement of the catalysis of hydrogen peroxide in solutions of these salts, the author draws the following conclusions, in addition to those already published (see this vol., ii, 66): the compound Na_4UO_8 is probably a salt of a very weak acid having the constitution $\text{UO}(\text{O}_2\text{H})_3 \cdot \text{OH}$ or $\text{H}_4(\text{O}_2)_3\text{UO}_2$, and is very strongly hydrolysed in solution with formation of sodium hydroxide and hydrogen peroxide. KVO_4 is a salt of a monobasic acid, and $\text{K}_8\text{V}_5\text{O}_{26} \cdot \text{H}_2\text{O}$ a double compound of salts of a tetrabasic pyro-hyper-acid and of a monobasic meta-hyper-acid.

T. H. P.

Thorium Hydrogen, Thorium Rubidium, and Thorium Cæsium Sulphates. C. MANUELLI and B. GASPARINETTI (*Gazzetta*, 1902, 32, ii, 523—531).—The author gives new crystallographic measurements of the monoclinic, nona-hydrated thorium sulphate [$a:b:c = 0.599278:1:0.658937$; $\beta = 81^\circ 54' 27''$].

The hydrochloric acid solution of the products of fusion of the ashes of Auer gas mantles with three times their weight of sodium hydrogen sulphate deposits white crystals of the composition



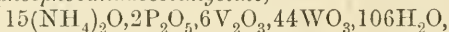
Thorium rubidium sulphate, $\text{Th}(\text{SO}_4)_2, \text{Rb}_2\text{SO}_4, 2\text{H}_2\text{O}$, and thorium cæsium sulphate, $\text{Th}(\text{SO}_4)_2, \text{Cs}_2\text{SO}_4, 2\text{H}_2\text{O}$, were also prepared.

T. H. P.

Derivatives of New Complex Inorganic Acids. ALLEN ROGERS (*J. Amer. Chem. Soc.*, 1903, 25, 298—315).—*Ammonium phosphovanadotungstate*, $13(\text{NH}_4)_2\text{O}, 2\text{P}_2\text{O}_5, 8\text{V}_2\text{O}_5, 34\text{WO}_3, 86\text{H}_2\text{O}$, prepared by boiling ammonium phosphate, ammonium vanadate, and ammonium tungstate with water, forms dark red crystals, very soluble

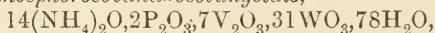
in water. When added to an aqueous solution of the tungstate, mercurous nitrate forms a yellow precipitate of mercury phosphovanadiotungstate, whilst silver nitrate gives a brick-red precipitate of the silver salt, $13\text{Ag}_2\text{O}, 2\text{P}_2\text{O}_5, 8\text{V}_2\text{O}_5, 33\text{WO}_3, 41\text{H}_2\text{O}$.

Ammonium phosphovanadosotungstate,



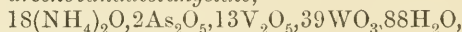
prepared in similar manner from vanadium trioxide, forms black crystals, which are partly octahedral, partly cubic.

Ammonium phosphorosovanadosotungstate,



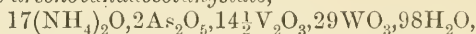
prepared from ammonium phosphite, vanadium trioxide, ammonium tungstate, and ammonia, forms black, octahedral crystals soluble in water.

Ammonium arsenovanadiotungstate,

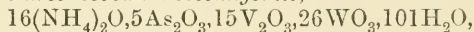


forms octahedral crystals soluble in water.

Ammonium arsenovanadosotungstate,

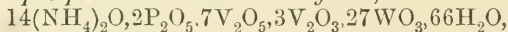


and *ammonium arsenosovanadosotungstate*,



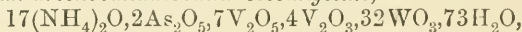
crystallise in black octahedra, sparingly soluble in cold water.

Ammonium phosphovanadiovvanadosotungstate,



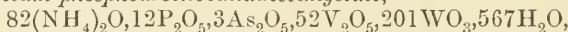
forms greenish-black octahedra, sparingly soluble in cold water.

Ammonium arsenovanadiovanadosotungstate,



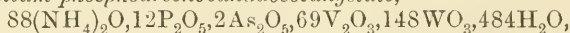
is black.

Ammonium phosphoarsovanadiotungstate,



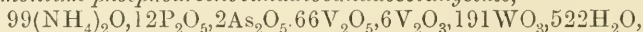
crystallises in dark red octahedra.

Ammonium phosphoarsovanadosotungstate,



forms greenish-black, octahedral crystals soluble in water.

Ammonium phosphoarsovanadiovvanadosotungstate,



forms black octahedra.

The author considers that the formulæ he has assigned to those various compounds cannot be regarded as being definite. A. McK.

Alums of Iridium Sesquioxide. L. MARINO (*Gazzetta*, 1902, 32, ii, 511—513).—The author has prepared an iridium rubidium alum by the following method. Concentrated iridium tetrachloride solution was reduced by the electric current yielding the sesquichloride which, on precipitation with potassium hydroxide free from alum, gave the hydrated sesquioxide. The latter was thoroughly washed out of contact with the air and dissolved in the minimum quantity of dilute sulphuric acid. The calculated amount of rubidium sulphate was then added and the liquid evaporated in a vacuum over sulphuric acid, by which means pale yellow octahedra having the composition

$\text{Ir}_2\text{Rb}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ were obtained. Both in the solid state and in solution, the alum remains unaltered in the air. T. H. P.

Mineralogical Chemistry.

Connection between the Molecular Volume and Chemical Composition of some Crystallographically Similar Minerals. GEORGE T. PRIOR (*Min. Mag.*, 1903, 13, 217—223).—The molecular volumes of the members of an isomorphous group of minerals show an approach to equality. In some other minerals, however, which are closely related crystallographically and have approximately equal molecular volumes, the chemical relationship is not so close; for example, calcite and sodium nitrate, with molecular volumes of 37 and 40 respectively, and albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), both with a molecular volume of 100. A similar relation is shown by the following group of rhombohedral phosphates and sulphates (compare Abstr., 1900, ii, 602):

	Formula.	$\gamma\gamma'$.	ϵ .	Mol. vol.
Hamlinite	$\text{AlPO}_4, \text{SrHPO}_4, \text{Al}_2(\text{OH})_6$	87° 2'	1·1353	142
Florencite	$\text{AlPO}_4, \text{CePO}_4, \text{Al}_2(\text{OH})_6$	88 56	1·1901	143
Svanbergite	$\text{AlPO}_4, \text{SrSO}_4, \text{Al}_2(\text{OH})_6$	89 25	1·2063	140
Bendantite	$\text{Fe}'''\text{PO}_4, \text{PbSO}_4, \text{Fe}_2(\text{OH})_6$	88 42	1·1842	155
Alunite	$\text{AlK}(\text{SO}_4)_2, \text{Al}_2(\text{OH})_6$	90 50	1·2520	150
Jarosite	$\text{Fe}'''\text{K}(\text{SO}_4)_2, \text{Fe}_2(\text{OH})_6$	90 45	1·2492	154
Natrojarosite	$\text{Fe}'''\text{Na}(\text{SO}_4)_2, \text{Fe}_2(\text{OH})_6$	85 54	1·1038	154
Plumbojarosite .. .	$\text{Fe}'''\text{Pb}_3(\text{SO}_4)_2, \text{Fe}_2(\text{OH})_6$	89 42	1·2156	154
Utalite	$2\text{Fe}''(\text{OH})\text{SO}_4, \text{Fe}_2(\text{OH})_6$	84 9	1·0576	—

Similar relations connecting crystalline form, molecular volume, and chemical composition are shown to exist between monazite (CePO_4) and crocoite (PbCrO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and brushite ($\text{HCaPO}_4 \cdot 2\text{H}_2\text{O}$), and many other pairs of minerals. In other cases, however, a similar relation is only obtained when some multiple of the simplest formula is taken, as in the following groups amongst others:

	Formula.	System.	Elements.	Mol. vol.
{ Zircon	ZrSiO_4	Tetragonal	1 : 0·6404	39
{ Rutile	TiTiO_4	,,	1 : 0·6442	38
{ Sellaite	MgMgF_4	,,	1 : 0·6596	41
{ Xenotime	YPO_4	,,	1 : 0·6187	41
{ Brookite	$\text{Ti}_2\text{Ti}_4\text{O}_{12}$	Orthorhombic	0·8416 : 1 : 0·9444	118
{ Tantalite	$\text{Fe}_2\text{Ta}_4\text{O}_{12}$,,	0·8285 : 1 : 0·8898	125
{ Hübnerite	$\text{Mn}_3\text{W}_3\text{O}_{12}$	Monoclinic	0·8300 : 1 : 0·8678 ; $\beta = 89^\circ 22'$	126
{ Celestite	SrSO_4	Orthorhombic	0·7789 : 1 : 1·2800	47
{ Marcasite	FeFeS_4	,,	0·7662 : 1 : 1·2342	50
{ Copper-pyrites..	$\text{Cu}_2\text{Fe}_2\text{S}_4$	Tetragonal	1 : 0·9853	88
{ Stannite	$\text{Cu}_2\text{FeSnS}_4$,,	1 : 0·9827	95
{ Calcite	$\text{Ca}_2\text{C}_2\text{O}_6$	Rhombohedral	1 : 0·8543	74
{ Nordenskiöldine	CaSnB_2O_6	,,	1 : 0·8221	65
{ Calomel	Hg_2Cl_2	Tetragonal	1 : 1·7229	72
{ Mallockite	$\text{Pb}_2\text{Cl}_2\text{O}$,,	1 : 1·7627	70
{ Anatase	Ti_4O_8	,,	1 : 1·7771	80

On these grounds, the formulæ of the polymeric minerals rutile, anatase, and brookite are written Ti_2O_4 , Ti_4O_8 , and Ti_6O_{12} respectively.

As in ordinary isomorphous groups, single elements may be termed crystallographically equivalent, so in the present cases groups of elements may be so considered; thus, CaC is equivalent to NaN , $NaSi$ to $CaAl$, &c. In many cases, however, in complex molecules, the small influence of certain elements or groups may depend on the "mass effect" (Abstr., 1899, ii, 305; 1902, ii, 667) of the other constituents of the molecule.

L. J. S.

Analysis of Zinc-blende from Russia. K. NENADKEWITCH (*Bull. Soc. Nat. Moscou*, 1903, 1902, 350—352).—Homogeneous, transparent cleavage fragments of large crystals of zinc-blende from Nagolnyj Krjasch gave:

Zn.	S.	Cd,Cu.	Fe.	Total.	Sp. Gr.
66.19	32.88	0.79	trace	99.86	4.0998

L. J. S.

Western Australian Tellurides: the non-existence of "Kalgoorlite" and "Coolgardite" as Mineral Species. LEONARD J. SPENCER (*Min. Mag.*, 1903, 13, 268—290).—The massive tellurides occurring in green sericite-schist at Kalgoorlie, Western Australia, include: calaverite ($AuTe_2$), sylvanite ($AuAgTe_4$), petzite (Ag_3AuTe_2), coloradoite ($HgTe$), and altaite ($PbTe$). Associated with these are sometimes fahlerz, magnetite, tourmaline, &c., and more frequently native gold. Gold in a fine state of division is also produced by the decomposition of the tellurides.

Analysis of carefully selected coloradoite gave: Hg, 60.95; Te, 39.38 = 100.33; sp. gr. 8.07. This agrees with the usually accepted formula, $HgTe$, and not with the formula Hg_2Te_3 , recently suggested by Simpson (Abstr., 1902, ii, 510).

Coloradoite is of frequent occurrence, and is often intimately associated with petzite; both have the same iron-black colour and well-marked conchoidal fracture, and they can only be distinguished by chemical tests. "Kalgoorlite" (Abstr., 1898, ii, 385) described as having these physical characters is thus, without doubt, a mixture of coloradoite and petzite. In the same way, "Coolgardite" (Abstr., 1901, ii, 515) is shown to be a mixture of coloradoite with calaverite, petzite, and sylvanite.

L. J. S.

Minerals from Skye and Ross-shire. WILLIAM POLLARD (*Summ. Prog. Geol. Survey United Kingdom*, for 1901, 1902, 86—87).—Small, lustrous octahedra of a black spinel constitute practically the whole of certain seams in banded dunite near Loch Scavaig, Skye; the following analysis proves it to be picotite:

SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	Cr_2O_3 .	FeO .	MnO .	$(Co,Ni)O$.	CaO .	MgO .	Total.
1.19	0.34	46.54	6.01	17.55	10.10	trace	0.24	0.43	18.35	100.75

The felspathic constituent of a nepheline-ægirine-syenite-pegmatite, found as a boulder at Coulmore, Ross-shire, gave :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.
63·84	18·87	0·68	0·18	14·76	1·23	0·30	99·86

L. J. S.

Reduction of Oligist Iron to Magnetite by Hydrocarbons. L. DE LAUNAY (*Compt. rend.*, 1903, 135, 406—408).—From observations made in the mines of Grängesberg, Sweden, the conclusion is drawn that oligist iron has been produced from magnetite by the reducing action of the bituminous substances associated with quartz veins.

The possibility of such a reduction was shown by an experiment in which yellow hæmatite was heated at 250° with petroleum. Red hæmatite containing an appreciable amount of magnetite was produced.

N. H. J. M.

Meigen's Method of Discriminating Calcite and Aragonite. ARTHUR HUTCHINSON (*Min. Mag.*, 1903, 13, Proc., xxviii).—Experiments were made in order to discover the cause of the discrepancy in the results obtained by Meigen (*Abstr.*, 1901, ii, 692) and G. Panebianco (*Riv. Min. Crist. Ital.*, 1902, 28, 5—12) in the application of Meigen's method for discriminating between calcite and aragonite. It was found that calcite, when treated with a boiling dilute solution of cobalt nitrate, only remains white or becomes yellow (as stated by Meigen) when the cobalt nitrate contains traces of iron, and that Panebianco's lavender-blue colour is only obtained when the cobalt nitrate is free from iron.

L. J. S.

Pseudogaylussite from the Clyde. JOHN S. FLETT and WILLIAM POLLARD (*Summ. Prog. Geol. Survey United Kingdom*, for 1901, 1902, 89—91. Compare *Abstr.*, 1902, ii, 89).—Long, prismatic crystals of a dark brown colour and square or rhombic cross-section were dredged from the Clyde, near Helensburgh. Thin sections under the microscope showed them to consist of small spherules of fibrous calcite. Analysis gave :

CaO.	MgO.	CO ₂ .	P ₂ O ₅ .	Fe, Mn, Cl, SO ₃ .	Loss at 105°.	Loss on ignition.	Insol. in HCl.	Total.	Sp. gr.
47·93	4·21	39·91	2·23	traces	3·13	2·81	0·11	100·33	2·56

L. J. S.

Artinite, a New Mineral. LUIGI BRUGNATELLI (*Rend. Ist. Lombardo*, 1902, [ii], 35, 869—874; *Centr. Min.*, 1903, 144—148).—A more detailed examination has been made of the hydrated basic magnesium carbonate (*Abstr.*, 1899, ii, 372) from the asbestos mines in the Val Lanterna, Val Tellina, Lombardy, and the new name artinite is now given. It occurs in peridotite as loose aggregates of snow-white scales, which are composed of minute, prismatic crystals.

The optical characters agree with orthorhombic symmetry. Analysis gave: MgO , 41.34; CO_2 , 22.37; H_2O , 34.90 = 98.61, corresponding with the formula $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. In composition, the mineral is thus near to hydrogiobertite, which, however, is shown to be a mixture of at least two minerals.

L. J. S.

Composition and Optical Characters of Chalybite from Cornwall. ARTHUR HUTCHINSON (*Min. Mag.*, 1903, 13, 209—216).—The material examined consisted of crystals from Camborne, which, when broken up, yielded perfectly transparent cleavage fragments of a pale yellow colour. Analysis gave the following results, corresponding with 98.43 per cent. of FeCO_3 :

FeO .	MnO .	CaO .	MgO .	CO_2 .	Total.	Sp. gr.
61.08	1.12	0.10	0.13	38.19	100.62	3.037

Careful determinations were made of the refractive indices; for sodium-light, $\omega = 1.8724$, $\epsilon = 1.6338$.

L. J. S.

Serendibite, a New Boro-silicate from Ceylon. GEORGE T. PRIOR and ANANDA K. COOMARASWAMY (*Min. Mag.*, 1903, 13, 224—227).—A preliminary account of the characters and occurrence of this new mineral has already been given (Abstr., 1902, ii, 567).

L. J. S.

[Roscoelite from Western Australia.] RICHARD PEARCE (*Proc. Colorado Sci. Soc.*, [1902] (Read October 2, 1897), 6, 69—72).—A specimen of telluride gold ore from Kalgoorlie showed the presence of a dark green talcose mineral. The portion of the heavy residue insoluble in aqua regia gave the following results on analysis, indicating the presence of roscoelite:

SiO_2 .	Fe_2O_3 .	Al_2O_3 .	CaO .	MgO .	V_2O_5 .
45.25	1.37	10.32	1.49	1.57	24.32

L. J. S.

Action of Ammonium Chloride on Silicates. FRANK W. CLARKE and GEORGE STEIGER (*Bull. U. S. Geol. Survey*, 1902, No. 207, 1—57).—A connected account is given of results previously published (Abstr., 1892, 772; 1900, ii, 24, 219, 414; 1902, ii, 269). The action of ammonium chloride at its temperature of dissociation on thirty-one mineral species is discussed. The influence of this reagent on various silicates differs very widely, but it appears to be much more powerful than has been generally supposed. The results are briefly as follows:

1. Analcite, leucite, natrolite, and scolecite, when heated with dry ammonium chloride at 350° in a sealed tube, yield alkali chlorides and an ammonium aluminium silicate, which is stable at 300° . The reaction is one of double decomposition, the sodium or potassium of the original silicate being replaced by ammonium. Analcite and leucite give the same product, $\text{NH}_4\text{AlSi}_2\text{O}_6$. Natrolite and scolecite yield the salt $(\text{NH}_4)_2\text{Al}_2\text{Si}_3\text{O}_{10}$. The constitution of the latter compound, a

derivative of orthotrisilic acid, $H_5Si_3O_{10}$, and its relations to other trisilicic acids, are considered.

2. A similar double decomposition occurs to a certain extent with stilbite, heulandite, chabazite, thomsonite, laumontite, and pollucite. Part of the monoxide base is removed and replaced by ammonium without change of atomic ratios. Cancrinite is vigorously attacked, and partially transformed into a zeolitic substance.

3. Pectolite, wollastonite, apophyllite, datolite, ilvaite, and calamine are violently acted on and their molecules, apparently, almost completely broken down. The products of the reactions are mixtures and no ammonium silicates are formed.

4. Elaeolite, sodalite, riebeckite, olivine, serpentine, phlogopite, prehnite, orthoclase, albite, oligoclase, aegirite, pyrophyllite, leuchtenbergite, and xanthophyllite are but slightly attacked.

In the closing section, it is shown that the ammonium chloride reaction may be applied to an approximate quantitative determination of analcite and leucite in rocks, thereby aiding somewhat in the estimation of their mineralogical composition.

L. J. S.

[Western Australian Minerals.] EDWARD S. SIMPSON (*Bull. Geol. Survey W. Austr.*, 1902, No. 6, 1—89).—An account of the results obtained, since 1897, in the laboratory of the Geological Survey of Western Australia includes numerous analyses of various minerals, waters, coals, rocks, &c., and assays of ores, some of which have been previously published (Abstr., 1901, ii, 454; 1902, ii, 509).

Topaz (analysis I) of a sky-blue colour occurs as large masses in granite dykes a few miles west of the Londonderry gold-mine in the Coolgardie gold-field. Lepidolite (II, by C. G. Gibson), as large sheets of an amethystine colour, is associated with this topaz. Spodumene (III, by C. G. Gibson), as large, prismatic crystals of an apple-green colour, occurs in a granite dyke at Ravensthorpe :

	SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	K ₂ O.	Na ₂ O.	Li ₂ O.	H ₂ O.	Total, less F.	O for F.	Sp. gr.
I.	32.11	57.08	0.26	—	trace	—	—	—	0.78	17.86	100.59	3.60
II.	51.00	24.13	trace	1.20	trace	10.31	2.43	5.97	0.22	7.79	99.77	2.75
III.	61.94	26.48	1.82	trace	0.28	0.47	1.93	7.02	0.29	—	100.23	3.20

L. J. S.

Two New Mineral Compounds Analogous to Pyrophyllite. JÓSEF MOROZEWICZ (*Tsch. Min. Mitth.*, 1903, 22, 97—102).—A mineral of an intense blue colour, resembling sodalite in appearance, occurs as veins in quartzite at Klutschi, government Orenburg. Under the microscope, thin sections show an aggregate of finely granular quartz and shreds of the strongly pleochroic blue mineral; the latter is not of one uniform colour, but is sometimes yellow. Analysis of the material separated by a heavy liquid gave the results under I. A second specimen of the rock treated in the same way gave the results under II. In both cases, the mineral is only slightly attacked by acids, even by a mixture of sulphuric and hydrofluoric.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.	Sp. gr.
I.	59·24	0·23	33·87	1·04	0·67	0·20	0·34	1·39	3·08	100·06	72·8	
II.	72·27	trace	24·15	0·75	—	0·25	0·56	1·35	1·66	100·99	2·869	

These analyses give the formulæ $2(\text{H}, \text{Na})_2\text{O}, 3\text{Al}_2\text{O}_3, 9\text{SiO}_2$ and $(\text{H}, \text{Na})_2\text{O}, 2\text{Al}_2\text{O}_3, 10\text{SiO}_2$ respectively; that is, aluminosilicic acids with part of the hydrogen replaced by metals. The minerals are thus related to, but not identical with, pyrophyllite ($\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$).

Other aluminosilicic acids of a similar nature probably remain to be discovered; the zeolites appear to represent hydrated salts of these acids. L. J. S.

Pyknochlorite, a New Chlorite, and other Minerals from the Radauthal, Harz. JOHANNES FROMME (*Tsch. Min. Mitth.*, 1903, 22, 62—73).—*Prehnite*.—Analysis I is of colourless to pale yellowish-green crystals from the pegmatite of the “Köhlerloch”; II, of compact masses and crystals of the same colour filling veins in gabbro on the Radauberg:

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
I.	43·53	24·18	0·88	27·20	trace	4·25	100·04	2·925
II.	44·00	23·68	0·90	26·30	0·34	4·58	99·80	2·919

The kind of rock in which the prehnite occurs has thus little or no influence on the amount of magnesia present, as might be supposed to be the case from earlier analyses.

Titaniferous Garnet.—An enclosed block, doubtless, originally of limestone, in the gabbro of Schmalenberg, consists of rounded garnets of the size of a walnut set in a pale canary-yellow ground-mass resembling idocrase, together with some calcite and green augite and wollastonite. The garnets consist of a blackish-brown nucleus (analysis III) surrounded by a lighter brown portion. The canary-yellow ground-mass (analysis IV) agrees approximately with idocrase in composition.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O, Na ₂ O.	Loss on igni- tion.	Total.	Sp. gr.
III.	37·42	1·29	17·92	5·98	2·64	0·87	34·00	trace	—	—	100·12	3·675
IV.	39·29	—	11·77	3·11	2·22	trace	33·97	6·85	0·13	2·75	100·09	3·356

Pyknochlorite.—This new chloritic mineral forms the cementing material of a brecciated vein of calcite and quartz in the gabbro of the Schmalenberg; it is of a greyish-green colour and compact texture. The reaction with acids is rather different in different specimens. Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O, Na ₂ O.	H ₂ O.	Total.	Sp. gr.
26·55	16·91	2·04	25·29	0·46	0·70	15·88	trace	12·06	99·89	2·831

In accordance with Tschermak's theory of the chlorite group, this analysis gives the same general formula, Sp_3At_4 , as for clinochlore, but the present mineral differs from this in the large amount of ferrous iron it contains and also in texture.

The decomposition of the gabbro follows two types: (1) ordinary weathering and oxidation of the rock with the formation of zeolites, &c.; (2) decomposition in the absence of free oxygen (the oxygen of percolating water having been retained by the humus of the overlying soil), with formation of chlorites. Some other minerals from the Radauthal are briefly described.

L. J. S.

Analysis of Garnet-sand from Lake Baikal. IN. BAGASCHOFF (*Bull. Soc. Nat. Moscou*, 1903, 1902, 329—334).—Sand from Olchon island, Lake Baikal, consisting of fine grains of a pale rose-red colour, gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Mn ₂ O ₃ .	FeO.	CaO.	MgO.	Total.	Sp. gr.
36·975	17·872	0·611	4·217	37·150	1·567	3·496	101·888	4·148

These results agree more closely with the garnet formula when the manganese is calculated as sesquioxide rather than as monoxide; in some other garnet analyses, the reverse is the case.

L. J. S.

Rottenstone from South Wales. WILLIAM POLLARD (*Summ. Prog. Geol. Survey United Kingdom*, for 1901, 1902, 80—83).—The following analyses by Cantrill are given: I, black, fine-grained limestone from the Tawe valley; II, inferior quality rottenstone; and III, best quality rottenstone from the same locality. The residues (18·75, 85·18, and 88·65 per cent. respectively) insoluble in dilute hydrochloric acid had the composition given under Ia, IIa, and IIIa.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.
I.	16·50	0·07	1·25	0·50	44·00	0·69	trace	0·32
II.	70·87	0·55	9·78	4·61	1·60	1·32	0·56	2·43
III.	80·82	0·29	5·82	3·79	1·43	0·88	0·30	1·40
Ia.	88·14	0·39	6·75	2·58	0·12	0·73	trace	1·70
IIa.	83·20	0·64	10·36	1·92	0·23	0·89	—	—
IIIa.	91·17	0·33	6·01	0·69	0·65	0·70	—	—

	CO ₂ .	P ₂ O ₅ .	FeS ₂ .	H ₂ O at 105°.	Loss on ignition.	Total.
I.	34·86	0·36	0·32	0·17	1·31	100·35
II.	0·27	1·39	—	2·18	4·62	100·18
III.	—	1·36	—	1·27	2·82	100·18

Rottenstone is thus the siliceous material left behind when limestone is weathered.

L. J. S.

Weathering of Magnesian Limestone. WILLIAM POLLARD (*Summ. Prog. Geol. Survey United Kingdom*, for 1901, 1902, 83—86. Compare Proc., 1901, 17, 201).—The black scale from the exterior of the Museum of Practical Geology gave, on analysis:

CaO.	MgO.	(Fe, Al) ₂ O ₃ .	SO ₃ .	CO ₂ .	Loss on ignition			Insol.	Total.
					H ₂ O at 105°.	H ₂ O 105—150°.	(H ₂ O and organic matter).		
26.9	9.5	1.4	20.7	19.4	1.8	9.1	6.5	5.2	100.5

The weathering of the dolomite exposed to the London atmosphere has thus given rise to calcium and magnesium sulphates. Crystals of gypsum up to 3 mm. in length were observed. L. J. S.

Physiological Chemistry.

Estimation of Calorific Value by means of Elementary Composition. ERWIN VOIT (*Zeit. Biol.*, 1903, 44, 345—361).—The calorific value of food materials can be calculated from their oxygen capacity; the numbers so obtained differ but little from those which are the result of direct experiment. W. D. H.

Calorific Value of Oxygen. OTTO KRUMMACHER (*Zeit. Biol.*, 1903, 44, 362—375).—In continuation of E. Voit's work (see preceding abstract), it is shown that the same method can be applied not only to chemical individuals, but also to mixtures. W. D. H.

Influence of Alcohol on Proteid Metabolism. RUDOLF ROSEMAN (Pflüger's *Archiv*, 1903, 94, 557—592. Compare Abstr., 1901, ii, 668).—A critical account of the researches of Chauveau, Kassowitz, Offer, Ott, and of Atwater and Benedict, all of which have been published since the author's previous paper. Most of this subsequent work confirms the contention that alcohol is a proteid-sparing food. W. D. H.

Changes in the Muscles of Warm-blooded Animals by Deprivation of Oxygen. CAMILL LIOTÁK VON LIOTA (*Pflüger's Archiv*, 1903, 94, 622—639).—Want of oxygen rapidly lowers the excitability of the muscles of warm-blooded animals. This accounts for the loss of excitability observed in asphyxia. Nevertheless, the muscles will sometimes execute a certain number of contractions after cessation of the heart. A certain degree of restoration can be brought about by mechanical means, but especially by a fresh supply of arterial blood. The muscles of weakly animals are not so markedly affected. W. D. H.

Glycogen of the Foetal Liver. EDUARD PFLÜGER (*Pflüger's Archiv*, 1903, 95, 19—22).—Bernard stated that in the first half of foetal life the liver contains no glycogen, although this substance is present in large quantities in other tissues. The new method now

adopted of preparing glycogen renders a reinvestigation of this statement necessary. The embryos used were those of calves, lambs, and pigs. The liver is usually poor in glycogen, but it is never completely free from that substance. W. D. H.

Identity of the Cholesterol from Milk with that from Bile. ANGELO MENOZZI (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 126—131).—By studying the optical properties of the cholesterol obtained from milk and from bile together with the optical and crystallographic properties of the formyl, acetyl, and benzoyl derivatives, the author finds that the two compounds are identical. T. H. P.

Presence of Dextrose in the Cephalorachid Liquid. LÉON GRIMBERT and V. COULAUD (*Compt. rend.*, 1903, 136, 391—392).—The reducing substance in human cephalorachid liquid, supposed by some to be dextrose and by others to be catechol, was identified by means of its osazone as dextrose. N. H. J. M.

Action of Secretin. C. FLEIG (*Compt. rend.*, 1903, 136, 464—466).—The main facts described by Bayliss and Starling are confirmed. In support of the suggestion that this substance acts on the secretory nerve-endings and not on the secretory cells of the pancreas, the experiments of Camus and Gley are quoted, which showed a certain degree of antagonism between atropine and small doses of secretin. W. D. H.

The Yellow Colour of the Skin in cases of Jaundice in which the Urine is free from Bile-pigment. F. H. THIELE (*Trans. Path. Soc. London*, 1903, 54, 62—68).—Many cases of jaundice are not associated with the presence of bile-pigment in the urine. The urine generally contains excess of urobilin, but this is not proportional to the depth of the jaundice; the yellow colour of the skin, blood serum, and tissues is, however, due to bilirubin. Bile-pigment must probably reach a definite percentage in the blood before it passes into the urine; it is not probable that it is converted into urobilin by the kidney in the process of excretion. So-called "urobilin jaundice" is regarded as true jaundice. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Bacterial Flora of London Air. F. W. ANDREWES (*Trans. Path. Soc. London*, 1903, 54, 43—48).—In an exhaustive examination of the bacteria, yeasts, moulds, &c., of London air, the remarkable chemical inertness of those found is striking. No truly pathogenic organism was found; hardly any coagulated milk, or formed acid, and none formed gas in dextrose-gelatin cultures. W. D. H.

Decomposition of Fodder and Foods by Micro-organisms. IV. Decomposition of Vegetable Foods by Bacteria. JOSEF KÖNIG, ALB. SPIECKERMANN, and A. OLIG (*Zeit. Nahr. Genussm.*, 1903, 6, 193—217. Compare Abstr., 1901, ii, 676; 1902, ii, 686; and 1903, ii, 169).—The bacteria capable of fermenting sugar belong entirely to the type *Bacillus coli communis* Escherich. In a 10 per cent. dextrose solution, they form succinic acid together with small quantities of formic acid, acetic acid, acetaldehyde, and esters. In 14 days, at 25°, the amount of alcohol produced was from 1.2 to 2.0 per cent. by weight. Some of them decompose proteids and pentosans to a small extent. Sugar is converted by *cocci* into acid substances. In the case of cotton-seed meal, the soluble carbohydrates prevented the decomposition of proteids by anaërobic bacteria, the acidity produced during the fermentation stopping the growth of the bacteria.

W. P. S.

Results obtained by the employment of *Saccharomyces* Acclimatised to the Volatile Toxic Substances Present in Beet Molasses. HENRI ALLIOT (*Compt. rend.*, 1903, 136, 510—511).—The results hitherto obtained show that it is possible to obtain purely alcoholic fermentation in presence of noxious chemical and bacterial impurities. The method effects an economy in calories, in refrigerating water, and in time. The yield of alcohol is as good as in the case of the old methods.

N. H. J. M.

Resistance of *Staphylococcus Pyogenes Aureus* to Mercury Perchloride. F. W. ANDREWES (*Trans. Path. Soc. London*, 1903, 54, 74—78).—Addition of 1 part of mercuric chloride to 1000 of culture broth does not prevent the growth of this organism. This is also true for mercuric iodide. The resistance of the organism to mercuric salts is described as specific.

W. D. H.

Behaviour of Yeasts in Mineral Solution. ALEXANDER KOSSOWICZ (*Chem. Centr.*, 1903, i, 475; from *Zeit. Landw. Versuchswes. Oesterr.*, 6, 27—59).—In mineral solutions containing only sugar, yeast increases only slowly and without visible evolution of carbon dioxide. Fermentation takes place, however, in such solutions when commercial sugar is employed, owing no doubt to the impurities present. Potassium salts, in considerable quantity, delay fermentation, but yeast becomes accustomed to moderately large amounts, whilst smaller amounts even promote fermentation. Variations in the amount of potassium present, such as occur in practice may have a decided influence on the fermentation.

N. H. J. M.

Development of Yeast in Sugar Solutions without Fermentation. D. IWANOWSKI (*Centr. Bakt. Par.*, 1903, II, 10, 180—183, and 209—214. Compare this vol., ii, 319, and A. Brown, *Trans.*, 1894, 65, 916).—A further reply to A. Richter (*loc. cit.*). Reference is made to previous experiments, which showed that yeast can consume sugar almost without alcoholic fermentation provided that, in addition to

free aëration, the nutritive solution is suitable in composition and contains only about 0.5 per cent. of sugar.

N. H. J. M.

Action of Certain Metallic Salts on the Growth of Micro-organisms. DAVID NABARRO (*Trans. Path. Soc. London*, 1903, 54, 48—61).—The salts mainly used were nickel chloride and copper sulphate. A large number of micro-organisms were investigated, and addition of these salts in varying amounts to the cultures inhibited their growth in different degrees.

W. D. H.

The Inhibitory Effect on Bacterial Growth of the Viscid Exudation obtained from Tabetic Joints. C. G. SELIGMANN (*Trans. Path. Soc. London*, 1903, 54, 68—74).—It was noticed that open joint wounds in cases of tabes did not become septic, and that the viscid exudation removed from the joints did not putrefy after removal, and when various bacteria were added to it they did not grow. The substance to which the viscosity is due contains no phosphorus, but is a mucoid. On dilution, the viscid fluid loses much of its viscosity, and then readily putrefies. The inhibitory effect on bacterial growth is attributed, not to any chemical material in the exudation, but to its physical condition. Experiments with other viscid fluids, or culture media rendered viscid, confirm this view.

W. D. H.

Influence of a Momentary Increase in the Tension of Oxygen on the Respiration of Fruits containing Volatile Esters during the Period of Maturity in which they emit Perfume. C. GERBER (*Compt. rend. Soc. Biol.*, 1903, 55, 267—269).—A sudden and momentary increase in the tension of oxygen reduces the respiratory quotient of odoriferous fruits. The diminution in the fermentation quotient is due to the oxidation of the alcohols which are normally produced and which lead to the high value of the quotient CO_2/O_2 noticed in these fruits.

When the value of the respiratory quotient remains above unity, notwithstanding the increased tension of oxygen, the oxidation of alcohol is partial, whilst there is a greater production of volatile esters. If, however, the value of the quotient falls below unity, the alcohol is completely oxidised, and the aroma disappears or, at least, greatly diminishes.

N. H. J. M.

Respiration of Odoriferous Fruits at the Time of Complete Maturity when placed, in the Green and Odourless State, in Air Enriched in Oxygen. C. GERBER (*Compt. rend. Soc. Biol.*, 1903, 55, 269—271. Compare preceding abstract).—The effect of an increase in the tension of oxygen on the ripe fruit, still green and without odour, is the reverse of that observed when the fruit has acquired its perfume. The value of the respiratory quotient increases and has all the characters of a fermentation quotient.

The prolonged increase in the tension of oxygen expedites the maturation of the fruits.

N. H. J. M.

Anaërobic Metabolism of Higher Plants and its Relation to Alcoholic Fermentation. JULIUS STOKLASA, JOH. JELINEK, and EUGEN VITEK (*Beitr. chem. Physiol. Path.*, 1903, 3, 460—509).—The results of experiments with sterilised sugar-beet showed that, in complete absence of micro-organisms, an alcoholic fermentation takes place. The roots contain an invertase and an enzyme very similar to zymase. Both enzymes are produced in absence of air.

The amount of carbon dioxide produced in anaërobic transpiration is only about 50 per cent. of that produced normally, a portion of the carbon being presumably utilised in the production of new constituents of the living protoplasm. N. H. J. M.

Occurrence of Salicylic Acid in Fruits. F. W. TRAPHAGEN and EDMUND BURKE (*J. Amer. Chem. Soc.*, 1903, 25, 242—244).—Salicylic acid seems to be constantly present in very small amount in fresh fruits. The fruit was distilled in each case with phosphoric acid and the distillate examined for salicylic acid. A. McK.

Enzymes of the Tea Leaf. HAROLD H. MANN (*J. Asiatic Soc. Bengal*, 1901, 70, 154—166).—The oxydase of tea leaves is most active below 55° and is destroyed at about 80°; it is very sensitive to acids and alkalis. The oxydase occurs chiefly in the unopened tip leaf of the shoot and in the stems; the amount diminishes as the leaf gets older.

Leaves grown under similar conditions yield the most highly flavoured tea when the amount of enzyme is greatest, and the amount of enzyme seems to be connected with the proportion of phosphoric acid in the soil. The quantity of enzyme in leaves increases materially during withering.

The small amount of starch present in tea leaves remains during withering, but disappears during fermentation. N. H. J. M.

Some of the Compounds present in American Cheddar Cheese. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Bull. New York Agric. Expt. Stat.*, No. 219, 1902, 203—216. Compare this vol., i, 215).—All the cheeses examined contained paranuclein. Cheese 4½ months old contained lysatine, histidine, and lysine; after 15 months, tetramethylenediamine and lysine were found.

Arginine could not be detected and guanidine was not looked for. Winterstein and Thöny's results (*Abstr.*, 1902, ii, 687) indicate that guanidine probably occurs in Emmenthaler cheese, which also contains pentamethylenediamine, a reduction product of lysine (Etlinger, *Zeit. physiol. Chem.*, 1900, 29, 334).

It seems probable that, in the ripening of hard cheeses, a conversion of primary into secondary amino-compounds takes place and that the flavour of normal cheese depends on these changes.

Cheese ripened at temperatures above 16—18° contains considerable quantities of ammonia.

The gases produced in "gassy" cheese consist partly of hydrogen. N. H. J. M.

Analytical Chemistry.

Improved Apparatus for Accurate Gas Analysis. WILLIAM H. SODEAU (*J. Soc. Chem. Ind.*, 1903, 22, 187—191).—The measuring tube has at the top a cylindrical bulb of 26 mm. internal diameter, joined to a capillary tube. Below the bulb is a straight stem graduated from 35 c.c. to 50 c.c. in 0.1 c.c. divisions. The capillary tube is bent at right-angles and is provided with a three-way stop-cock, the zero point of the graduation being at that side of the stop-cock furthest from the measuring tube. A small U-tube is connected with the branch of the stop-cock not in connection with the measuring tube, and serves for collecting the mercury employed for cleaning absorbents out of the capillary tube. The bottom of the measuring tube is connected to a side piece on the levelling tube. The latter, at its lower end, is joined to a T-piece, one branch of which is in connection with the mercury reservoir, and the other with a length of india-rubber tubing capable of being compressed by means of a screw clip. This serves as a fine adjustment for levelling the mercury after cutting off the reservoir by a stop-cock. The measuring and levelling tubes, as well as a "Kew principle" correction tube, are enclosed in a water-jacket. The pipettes for absorbents are horizontal, cylindrical bulbs and are joined to the capillary of the measuring tube by a piece of pressure tubing, a second three-way stop-cock being placed between the joint and pipette. The other branch of this stop-cock connects with a small mercury reservoir. The levels are read by means of a telescope. W. P. S.

Report of the Committee on Indicators. GEORG LUNGE (*Zeit. angew. Chem.*, 1903, 16, 145—148).—The choice of the committee has fallen on phenolphthalein for the titration of the organic acids and on methyl-orange for the titration of mineral acids and alkali hydroxides or carbonates. Methods for the estimation of alkali silicates, borates, and aluminates will be published later on.

L. DE K.

Volumetric Estimation of Free and Combined Sulphuric Acid. GUSTAV FRERICHS (*Arch. Pharm.*, 1903, 241, 159—160).—The method is similar to that recently proposed for the estimation of selenium (this vol., ii, 327); it is based on the fact that silver sulphate is insoluble in alcohol, whereas the nitrate is soluble. The solution, neutralised if necessary, is mixed with excess of silver nitrate and evaporated to dryness; the residue is powdered with a few drops of 95 per cent. alcohol, brought on to a filter, and washed with alcohol until the filtrate gives at most a very faint opalescence with hydrochloric acid. The residue on the filter is brought into a beaker, and mixed with about 10 c.c. of dilute nitric acid and 100 c.c. of water; the

whole is heated for about 5 minutes until the silver sulphate has dissolved, cooled a little, mixed with some iron alum solution, and titrated with $N/10$ potassium thiocyanate solution; 1 c.c. of this corresponds with 0.0040 gram of SO_3 , or 0.0049 gram of H_2SO_4 .

Sulphur in an organic compound can be estimated by this method, which also permits of the estimation of sulphur and halogens in one operation. The procedure is quite similar to that adopted in the case of selenium. C. F. B.

Gravimetric Estimation of Selenium. ALEXANDER GUTBIER and E. ROHN (*Zeit. anorg. Chem.*, 1903, 34, 448—452).—In aqueous solution, selenic acid is scarcely attacked by hypophosphorous acid. In neutral or acid solution, the reduction of selenium dioxide by hypophosphorous acids proceeds past the elementary stage and some hydrogen selenide is formed. In slightly alkaline solution, the reduction to the element takes place quantitatively, and the separated selenium can be collected and dried at 105° . If the selenium is originally in a higher state of oxidation, it must be reduced by boiling with hydrochloric acid until no more chlorine is evolved. J. McC.

Detection and Estimation of Ammonia in Waters by means of Diaminophenol. MANGET and MARION (*Ann. Chim. anal.*, 1903, 8, 83).—Diaminophenol (amidol) is recommended for the detection and colorimetric estimation of traces of ammonia in waters. It is said to be vastly superior to the Nessler reagent, showing very distinctly 1 part per million or even less. L. DE K.

Estimation of Citrate-soluble Phosphoric Acid. RUDOLF WOX (*Chem. Zeit.*, 1903, 27, 279—280).—Fifty c.c. of the usual solution in water containing 2 per cent. of citric acid are mixed with 30 c.c. of nitric acid of sp. gr. 1.15, 45 c.c. of ammonium nitrate solution (containing 340 grams per litre), and heated to boiling; 100 c.c. of a boiling 6 per cent. solution of ammonium molybdate are then added and the flame is removed. After 15 minutes, the clear liquid is passed through a Gooch crucible and the precipitate is washed with 50 c.c. of a "washing liquid" (50 grams of ammonium nitrate, and 40 c.c. of nitric acid per litre). The precipitate is now dissolved in 10 c.c. of 8 per cent. ammonia, 20 c.c. of ammonium nitrate solution, 30 c.c. of water, and 1 c.c. of molybdate solution are added, and after heating to boiling 20 c.c. of nitric acid are quickly introduced. The precipitate is now collected in the Gooch crucible, first washed with the "washing liquid," and finally with alcohol and ether. After removing this by suction, the crucible is placed inside a nickel crucible and gradually ignited until the mass has assumed a uniform bluish-black appearance. The precipitate then contains 3.946 per cent. of phosphoric oxide. L. DE K.

Estimation of Available Phosphoric Acid in Manures. WALTER F. SUTHERST (*Analyst*, 1903, 28, 66—71).—By extracting the fertiliser with successive fresh quantities of citric acid solution, thus approximately imitating the renewal of sap in roots, it was

found that practically the whole of the phosphoric acid was obtained from basic slag in five extractions and from coprolite (mineral phosphate) in eight extractions. Three grams of the fertiliser were treated with 300 c.c. of 1 per cent. citric acid solution each time, the duration of the extractions being 48 hours. Other experiments showed that potassium hydrogen oxalate and potassium hydrogen tartrate had about the same solvent action as citric acid, whilst potassium hydrogen malate was much weaker (compare Abstr., 1902, ii, 44).
W. P. S.

Estimation of Coal in Pyrites. FREDERICK P. TREADWELL and A. A. KOCH (*Zeit. angew. Chem.*, 1903, 16, 173—175).—Coal in pyrites may be estimated with sufficient accuracy by simply taking the loss on ignition and allowing for moisture and sulphur and also for the oxygen absorbed by the iron during the heating.

The amount of carbon may be approximately obtained by multiplying the percentage of coal thus found by 0.89.
L. DE K.

Estimation of Carbon Dioxide in the Carbonates of the Alkali and Alkaline Earth Metals by means of the Alkalimeter. S. FOKIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 76—78).—In estimating the carbon dioxide in salts of the alkali and alkaline earth metals or in minerals by treatment with an acid in an alkalimeter, the loss of weight of which is measured, the author finds that better results are obtained if phosphoric acid is used instead of hydrochloric or nitric acid. He recommends Rohrbeck's apparatus, about 1 gram of the substance being treated with 12 c.c. of a mixture of equal volumes of water and phosphoric acid. The evolution of the carbon dioxide is completed by boiling the solution, and both during and after the reaction dry air is kept passing through the apparatus.
T. H. P.

Influence of the Nature of the Cathode on the Quantitative Electrolytic Separation of Metals. AUGUSTE HOLLARD (*Bull. Soc. chim.*, 1903, [iii], 29, 217—221).—Advantage is taken of the relationship established by Caspari (Abstr., 1900, ii, 7) between the polarisation tension of hydrogen and the nature of the cell cathode to separate, even in acid solutions, metals having but slightly different electric tensions.

The cell is arranged so that both the cathode and the metal eventually deposited on this, lower the polarisation tension of hydrogen, thus, for the separation of cadmium and zinc, cathodes of cadmium or tin are employed. A number of results, illustrating the accuracy with which cadmium may be thus separated from zinc, are tabulated in the original.
T. A. H.

Application of Hydrofluoric Acid in Iron Works Laboratories. RUDOLF FRIED (*Zeit. angew. Chem.*, 1903, 16, 176—181).—The addition of a little hydrofluoric acid is recommended when dissolving samples of iron in nitric acid for the purpose of analysis. The amount of acid to be

added depends on the probable amount of silicon present; for instance, 1 c.c. is sufficient for 1 gram of ferro-silicon.

Although the beakers become somewhat unsightly, they are scarcely acted on by this treatment, and may be used repeatedly.

L. DE K.

Rivot's Quantitative Estimation of Iron in Presence of Zirconium. KARL DANIEL and HANS LEBERLE (*Zeit. anorg. Chem.*, 1903, 34, 393—402).—According to Rivot, iron may be quantitatively estimated in a mixture of ferric oxide with the oxides of zirconium, beryllium, chromium, tin, or silicon by reduction in a current of hydrogen, but the accuracy depends on the proportions of the oxides present.

Various mixtures of the oxides of iron and zirconium have been examined. The reduction to metallic iron is in no case complete, and as the proportion of zirconium oxide increases, the amount of ferric oxide which remains unreduced also increases. In all cases, the reduced product was pyrophoric, and this necessitated its being transferred to a weighing bottle from the ignition tube without coming into contact with the air.

Gutbier and Hüller's results (Abstr., 1902, ii, 701) with ferric and aluminium oxides have not been confirmed. In this case, the authors find the same discrepancy as with zirconium oxide, and they cannot explain Gutbier and Hüller's results by the supposition of a compensation of two errors acting in the opposite sense.

The authors discuss the principle of Rivot's process with reference to its use as an analytical method.

J. McC.

Elimination and Estimation of Manganese in Certain Products. M. EMM. Pozzi-Escot (*Ann. Chim. anal.*, 1903, 8, 88).—Manganese may be eliminated from technical products, for instance, aromatic acids, by cautious addition of hydrogen peroxide. Ammonium persulphate has also proved very useful.

L. DE K.

The Causse Tests for Water Pollution. SAMUEL RIDEAL (*J. Sanitary Inst.*, 1902, 23, 505—507).—Causse's test for polluted water—crystal-violet (hexamethyltriaminotriphenylcarbinol) bleached by sulphurous acid—was found to be quite untrustworthy (compare Abstr., 1901, ii, 581). The author considers the restoration of colour, in the case of pure water, to be due to the removal of free sulphurous acid, either by oxidation or neutralisation, and to be no indication of the purity of a water. On this account, further examination of Causse's method for estimating organic nitrogen (compare Abstr., 1902, ii, 584) was not considered to be necessary.

W. P. S.

Estimation and Separation of Cyanates, Cyanides, Thiocyanates, and Sulphides. J. MILBAUER (*Zeit. anal. Chem.*, 1903, 42, 77—95).—A Wurtz flask is fitted with a stop-cock funnel, the stem of which reaches the bottom of the flask; the side-tube is connected with a vertically-placed, bulbed Allihn condenser, the lower

end of which dips into strong potassium hydroxide solution. The flask is charged with a solution of potassium hydrogen sulphate and cadmium sulphate, which is boiled until the air is expelled from the apparatus. The mixed solution to be analysed is then added through the funnel at such a rate that the evolved gases are completely absorbed by the alkali. The sulphide present is converted into cadmium sulphide, the cyanide evolves hydrogen cyanide, the cyanate is hydrolysed to ammonium sulphate and carbon dioxide, the thiocyanate is left unchanged. After boiling for half an hour, these reactions are complete. The cadmium sulphide is collected on a Gooch filter, the filtrate being received in a second Wurtz flask. Addition of a little ether assists the filtration. The condenser is rinsed out and the cyanide in the distillate is titrated by Liebig's method after adding a drop of potassium iodide. The second Wurtz flask is now connected with the condenser. Alkali is run in through the funnel and the ammonia is distilled over into *N*/10 sulphuric acid. Finally, the thiocyanate is titrated by either Volhard's or Henriques' method. The results are excellent. A control may be obtained by estimating the total nitrogen of the mixed substances by Kjeldahl's process; this method becoming practicable after adding formaldehyde, to convert the cyanide into hydroxyacetonitrile. M. J. S.

Detection of Methyl Alcohol in Absinths. SANGLÉ-FERRIÈRE and L. CUNIASSE (*Ann. Chim. anal.*, 1903, 8, 82—83).—Fifty c.c. of the distilled sample are mixed with 1 c.c. of sulphuric acid, and 5 c.c. of a saturated solution of potassium permanganate are then added. If, after a few minutes, the permanganate colour persists, this should be destroyed by adding a drop or two of tannin solution.

The liquid is then rendered faintly alkaline with sodium carbonate and filtered. To the filtrate are then added 2 c.c. of a solution of phloroglucinol (1:1000) and 1 c.c. of strong aqueous potassium hydroxide, which will give a dark red colour if methyl alcohol is present.

The alkaline filtrate may also be acidified with dilute sulphuric acid, a few centigrams of gallic acid then added, and when dissolved, strong sulphuric acid poured down the sides. A blue ring indicates methyl alcohol. The two reactions depend on the formation of formaldehyde in the oxidation of methyl alcohol. L. DE K.

Degree of Acidity and other Analytical Data of various Wheaten Flours. ARNALDO FACHINATO (*Gazzetta*, 1902, 32, ii, 543—555).—The author has made a number of analytical determinations of wheaten flours of widely varying qualities in order to obtain data for the evaluation of such flours. The amount of moisture present does not vary much in different flours, and can only be used as a relative criterion. Of more value is a knowledge of the proportion of the flour soluble in water; and in the samples examined this proportion increases from 3.52 to 14.4 per cent. as the quality of the flour becomes lower. The most certain criterion, however, is the degree of acidity of the aqueous extract, or better, of the alcoholic (85° strength) extract of the flour; alcohol of this concentration

prevents the growth of micro-organisms, which sometimes cause a considerable increase in the acidity of the aqueous extract. In the alcoholic extract, the acidity, expressed in mg. of potassium hydroxide per 100 grams of flour, varies regularly from 28 to 476 when phenolphthalein is used as indicator, and from 21 to 364 when litmus is employed. The determination is rapid and simple and gives more trustworthy results than those obtained from a determination of the ash of the flour.

T. H. P.

Separation of Unsaturated Fatty Acids. K. FARNSTEINER (*Zeit. Nahr. Genussm.*, 1903, 6, 161—166).—Mainly controversial. The author maintains the accuracy of his method (compare Abstr., 1900, ii, 767) and gives the results of further estimations of the solubility of barium oleate in mixtures of alcohol and benzene. Estimations of oleic acid in various oils are also given.

W. P. S.

Estimation of β -Hydroxybutyric Acid in Urine. ERNST DARMSTAEDTER (*Zeit. physiol. Chem.*, 1903, 37, 355—362).—The transformation of β -hydroxybutyric acid into crotonic acid is quantitative when the hydroxy-acid is distilled with 50 per cent. sulphuric acid for several hours under such conditions that the concentration of the sulphuric acid is kept practically constant.

The method recommended is as follows: 100 c.c. of urine are rendered faintly alkaline with sodium carbonate and evaporated practically to dryness. The residue is mixed with 150—200 c.c. of 50—55 per cent. sulphuric acid in a litre flask fitted with a condenser and dropping funnel. The liquid is first heated gently to avoid frothing and then rapidly distilled, water being run in from the dropping funnel in order to keep the volume constant. The distillate, which should measure 300—350 c.c., is extracted with ether, the ether distilled, and the residue heated on the sand-bath at 160° in order to remove fatty acids, then dissolved in 50 c.c. of water, filtered, and the clear solution titrated with *N*/10 sodium hydroxide, using phenolphthalein as indicator. 100 c.c. of *N*/10 alkali are equivalent to 0.86 gram of crotonic or 1.0406 grams of hydroxybutyric acid.

J. J. S.

Detection of Salicylic Acid in Foods by the Ferric Chloride Test. HENRI TAFPE (*Ann. Chim. anal.*, 1903, 8, 84).—Light petroleum of sp. gr. less than 0.70 is now recommended for the extraction of acid solutions containing salicylic acid instead of the author's previous mixture of light petroleum and ether. No substances which interfere will then pass into solution.

L. DE K.

Detection of Heated Milk. FRANZ UTZ (*Milch. Zeit.*, 1903, 32, 129—131).—Schardinger's reaction (compare Abstr., 1903, ii, 190) was found to be untrustworthy, because even unheated milk, unless perfectly fresh, does not decolorise the methylene-blue solution. After rendering the milk feebly alkaline with milk of lime, it decolorises the methylene-blue, but boiled milk, when made alkaline, behaves in

exactly the same manner as unheated milk. The reaction in this case is probably due to the reducing powers of the sugars present.

W. P. S.

Detection of Fatty Oils by Micro-chemical Saponification. C. HARTWICH and W. UHLMANN (*Arch. Pharm.*, 1903, **241**, 111—115. Compare this vol., ii, 36).—Water is saturated with potassium hydroxide in the cold, and the solution mixed with an equal volume of 20 per cent. ammonia; three other solutions are prepared from this by diluting it respectively with one, two, and three times its volume of water. A drop of each of the four solutions is placed on an object glass, and a little of the oil is stirred into each drop with the point of a needle; the oil breaks up into tiny drops of different size. The mixtures are then covered with cover-glasses and examined, both in ordinary and in polarised light, at intervals during 3 days; generally, after 1 and $4\frac{1}{2}$ hours and 1 and 3 days. The potassium salt of the fatty acid separates either in definite crystals of varying configuration or in spherites, that is, spherical aggregates of tiny crystals which exhibit a dark cross in polarised light. The appearances obtained are described in the case of olive, almond, peach-kernel, arachis, linseed, poppy, and castor oils.

C. F. B.

Analysis of Aniline Oil by the Volumetric Method. W. G. SCHAPOSCHNIKOFF and SACHNOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 72—75).—The author gives an improved method of carrying out Reinhardt's process for estimating the aniline and toluidine in aniline oil, which depends on the bromination of these two amines by potassium bromate in hydrobromic acid solution; the reactions are as follows: $\text{NH}_2\text{Ph} \cdot \text{HBr} + 2\text{HBr} + \text{KBrO}_3 = \text{C}_6\text{H}_2\text{Br}_3 \cdot \text{NH}_2 + \text{KBr} + 3\text{H}_2\text{O}$, and $3\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2 \cdot \text{HBr} + 3\text{HBr} + \text{KBrO}_3 = 3\text{C}_6\text{H}_2\text{MeBr}_2 \cdot \text{NH}_2 + \text{KBr} + 6\text{H}_2\text{O}$. The potassium bromate used is the recrystallised commercial product of which an 8 per cent. solution is prepared, the strength being determined by mixing 25 c.c. with 5 grams of potassium iodide and 3 c.c. of 25 per cent. hydrobromic acid solution, and estimating, by titration with standard thiosulphate, the iodine set free according to the equation: $\text{KBrO}_3 + 6\text{HBr} + 6\text{KI} = 3\text{I}_2 + 7\text{KBr} + 3\text{H}_2\text{O}$. One gram of iodine corresponds with 0.22083 gram of potassium bromate, that is, with 0.12231 gram of aniline, or 0.14061 gram of toluidine. About 1 gram of the aniline oil is dissolved in about 60 grams of 25 per cent. hydrobromic acid solution, and the bromate solution run in until the clear liquid above the bromide precipitate assumes a yellow coloration. Then, if a is the weight of oil taken, n the number of c.c. of bromate solution employed, t_a and t_t the amounts of aniline and toluidine respectively corresponding with 1 c.c. of the bromate solution, the percentage of aniline in the oil is given by: $100t_a(nt_t - a)/a(t_t - t_a)$, and that of the toluidine by $100t_t(a - nt_a)/a(t_t - t_a)$.

T. H. P.

Evaluation of Ethyl- α - and β -naphthylamines. WILHELM VAUBEL (*Chem. Zeit.*, 1903, **27**, 278—279).—Commercial ethyl- α -naphthylamine has a sp. gr. 1.073, whilst the β -compound has a sp. gr. 1.062 at 18°. The former boils over a range of temperature from 292° to 323°, the

major part distilling at 310—323° under 745 mm. pressure; ethyl- β -naphthylamine boils between 322° and 336°, 50 per cent. distilling at the latter temperature. On attempting to estimate the amount of bromine absorbed when a solution of the α -base in acetic acid, to which sulphuric acid and potassium bromide have been added, is titrated with aqueous potassium bromate, it was found that 3 mols. of bromine disappeared for each 2 mols. of the base, but that of this 2 mols. were used in oxidising the amine, and only 1 mol. effected substitution. With ethyl- β -naphthylamine, on the other hand, 4 mols. of bromine disappeared for 2 mols. of the base, of which 3 mols. act as a substituting, and 1 mol. as an oxidising, agent. The addition of sulphuric acid to the α -derivative produces a precipitate, but not with the β -derivative; in the action of bromine on the α -derivative, an immediate purple-red coloration is developed; with the β -derivative, on the other hand, a green coloration is obtained.

K. J. P. O.

The Volumetric Estimation of Alkaloids. CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1903, 42, 101—108).—The author's experiments show that the results obtained by Gordin's method, whether using Wagner's or Mayer's reagent (*Abstr.*, 1900, ii, 119), are so profoundly influenced by the proportion of free acid, as well as by that of the potassium iodide in the solution, that they are useless for quantitative purposes, being not only far too high, but extremely irregular. Gordin's suggestion that the acid should be standardised by a known quantity of morphine is also found to be unserviceable, since equivalent quantities of morphine and strychnine titrated under identical conditions gave widely different results. It is further objected that many of the impurities which would inevitably be present in alkaloids obtained in the course of pharmaceutical or toxicological investigations would combine with some of the acid present and therefore be calculated as alkaloid.

M. J. S.

Estimation of Quinine in Mixtures of Cinchona Alkaloids, in Cinchona Bark, and in Galenical Preparations obtained from these. WALDEMAR HILLE (*Arch. Pharm.*, 1903, 241, 54—110).—The various methods of separating the alkaloids of cinchona bark and estimating the quinine have been examined. For details, the original paper must be consulted.

Treatment with Ether.—This does not permit of an accurate estimation of the quinine, for the accompanying alkaloids also go into solution to an appreciable extent. In order to dissolve 1 part of the respective alkaloids at the ordinary temperature, the following number of parts are required of (1) absolute ether, sp. gr. 0.718 at 17°; (2) ether containing 4 per cent. of alcohol, sp. gr. 0.726 at 15°; (3) ether saturated with water:

	Absolute ether.	Alcoholic ether.	Aqueous ether.
Quinine	46.5	10	19.8
Quinidine	57.8	40	69.4
Cinchonine	656	743	741
Cinchonidine	354	68	222

The alkaloids dissolve but slowly in ether at the ordinary temperature. Solutions made at a higher temperature easily remain supersaturated. In all cases, the alkaloids are much more soluble in ether just after they have been precipitated from solutions of their salts by means of an alkali. Under these circumstances, an extremely concentrated solution of quinine in alcoholic ether can be obtained, but the ether cannot be evaporated from this solution at a temperature as high as 60—80°. Although this method is useless for the estimation of quinine, it may be used to obtain from a given mixture of alkaloids a mixture richer in quinine (see next paragraph).

Herapathite Method of de Vrij.—This is one of the best methods. The correction for the solubility of the quinine herapathite (iodo-sulphate) in the mother liquor is 0.157 gram in 100, rather than 0.125. In two test experiments, the amount of quinine obtained was 100.1 and 101.5 per cent. of that taken. The result is inaccurate if the percentage of quinine in the mixture of alkaloids is less than 30, or perhaps 40. In this case, the mixture of alkaloids, after precipitation with sodium hydroxide, should be shaken with 15 c.c. of ether for a short time only, a few drops of ether added to expedite the separation of the layers, and the ethereal layer brought rapidly into a small flask; it is then shaken vigorously, when most of the alkaloids accompanying the quinine separate and can be filtered off, the filter being washed with ether. The alkaline solution is shaken four times more with 10 c.c. of ether. The ether is evaporated, and the residue, which contains all the quinine with comparatively little of the other alkaloids, can be treated by the herapathite method.

Oxalate Method of Shimoyama.—This is a good method, and in three test experiments the amount of quinine obtained was 100.7, 101.4, and 100.95 per cent. of that taken.

Polarisation Method.—This gives good results if the quinine is mixed with only one other alkaloid, the identity of which is known. If two other alkaloids are present, and still more with three, the error of the experiment is increased so largely in the calculation of the result that the latter may be quite erroneous.

Carles' Method.—Although quinine sulphate is practically insoluble in aqueous ammonium sulphate, a correction should be applied for the amount that dissolves in the water used for washing; this was found to be 0.0078 gram in 20 c.c. In a test experiment, the amount of quinine found was 101.9 of that taken.

Tartrate Method.—This method, as modified by J. H. Schmidt, is a good one.

Precipitation with Potassium Iodide.—The amounts of water required to dissolve 1 part of the alkaloid hydriodides at 18—20° are respectively 121, 1256, 97, and 75.8, taking the alkaloids in the same order as on p. 396. It is not possible to separate the alkaloids by this method, but use may be made of it to find whether a mixture of alkaloids contains more than 10 per cent. of quinidine; 0.5 gram of the mixture is dissolved in water containing some acid, the solution is neutralised, diluted to 65 c.c., and treated with 0.3 gram of potassium iodide; a white precipitate is obtained only when more than 10 per cent. of quinidine was present in the mixture.

Precipitation of the Nitroprussides.—To dissolve 1 part of the nitroprussides, 2757, 231, 211, and 482 parts of water at 18—20° are required, but a dilution of over 1:700 is necessary in order to prevent any precipitation of the alkaloids other than quinine when all three are present together, so that a convenient method of separation by means of these salts is out of the question.

Chromate Method.—To dissolve 1 part of the respective chromates, 2337, 230, 974, and 272 parts of water at 18—20° are necessary. The solution in which precipitation is effected should amount to 200 grams, and then a correct result will be obtained even if 0.2 gram of cinchonine is present, an amount never likely to be exceeded if 1 gram of the mixture of alkaloids is taken for analysis. The correction for solubility of the quinine salt should be 0.020 gram per 100 c.c. of mother liquor *plus* wash-water. In a test experiment, the amount of quinine obtained was 99.5 per cent. of that taken.

Precipitation of the Benzenethiosulphonates (Abstr., 1901, i, 338).—To dissolve 1 part of the respective salts, 5211, 654, 282, and 296 parts of water at 18—20° are necessary. The precipitates cannot be filtered quantitatively, however, and attempts to precipitate with excess of sodium thiosulphate and estimate the excess by titration with iodine gave unsatisfactory results.

Treatment with Ether saturated with the other Alkaloids.—This is a new method. In a room of constant temperature, quinidine, cinchonine, and cinchonidine are allowed to remain with ether and alcohol in the proportions 2.44:0.14:1.45:96:4 by weight during 1 to 2 days, the mixture being shaken frequently; the liquid is then withdrawn as required without filtration. The amount of alkaloids it contains varies considerably with the temperature; a table is given of the amount present in 25 c.c. of the saturated ether for every half degree between 8° and 20°; this amount is also given by the value of the expression $0.3857 + 0.00975(t - 14) + 0.0000625(t - 14)^2$. In an estimation, 0.5 gram of the mixture of alkaloids under examination is allowed to remain for an hour with 50 c.c. of the saturated ether in the room at constant temperature in a stoppered cylinder which is shaken frequently; the temperature is noted, and 25 c.c. are transferred with a pipette to a tared beaker and evaporated, and the residue is dried at 125—135° and weighed; its weight, less that of the alkaloids contained in 25 c.c. of the saturated ether at the temperature noted, gives the weight of quinine in the mixture. The method gives good results, the error only becoming appreciable when very little cinchonine and cinchonidine are present; moreover, it is the only method that gives good results when the amount of quinine is less than 20—30 per cent. of the total alkaloids. In 8 test experiments, the quantity of quinine found was 99.85, 99.3, 99.2, 100.9, 100.9, 100.3, 100.4, and 102.3 of that taken.

The herapathite, oxalate, and tartrate methods are probably the most accurate, but for approximate estimations the sulphate method is in general perhaps the most suitable. When the quinine amounts to less than 20 per cent. of the total alkaloids, however, the method with saturated ether is most convenient, and perhaps is so in all cases.

Analyses are given of a number of samples of cinchona bark; the percentage of quinine varied from 2.13 to 0.39, that of the total alkaloids from 5.5 to 3.0. Details are given for the estimation of quinine in extracts and tinctures as well as in barks. C. F. B.

A Proteid Reaction involving the use of Chromate. WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, xv—xvi; *Amer. J. Physiol.*, 8).—Solutions of chromates of uni- and bi-valent cations cause no precipitation in neutral or alkaline proteid fluids, but on the addition of small amounts of acids, especially strongly dissociable ones, flocculent precipitation of proteid-chromate occurs in every case; this is very striking with gelatin, also with proteoses (here the precipitate dissolves on warming and reappears on cooling). Dichromates without acid are as inert as chromates. Hydroxyl ions prevent the reaction in all cases. Possibly the reaction is due to the formation of dichromic acid, just as the acetic acid and potassium ferrocyanide test is due to the formation of hydroferrocyanic acid. W. D. H.

Estimation of Proteolytic Compounds in Cheese and Milk. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Amer. Chem. J.*, 1903, 29, ii, 150—170).—In order to estimate the various soluble nitrogenous principles in cheese or milk, advantage is taken of certain precipitants. The precipitates or resulting filtrates are then treated by the Kjeldahl-Gunning process. Addition of a small crystal of copper sulphate will facilitate the conversion of the nitrogen into ammonia, particularly when estimating the total nitrogen in cheese. Twenty-five grams of well-sampled cheese are mixed in a mortar with an equal bulk of clean quartz sand and extracted with 100 c.c. of water at 50—55° for half an hour. The liquid is poured off, and the extraction repeated several times, and finally the volume of the liquid (not counting any fatty layer) is made up to 500 c.c. The solution is then passed through a cotton filter.

Estimation of Total Water-soluble Nitrogen.—Fifty c.c. of the aqueous solution are used. **Estimation of Nitrogen in the Form of Paranuclein (Pseudonuclein).**—One hundred c.c. of the aqueous solution are mixed with 5 c.c. of a 1 per cent. solution of hydrochloric acid and coagulated at 50—55°. The nitrogen in the precipitate represents pseudonuclein. **Estimation of Nitrogen in the Form of Proteids Coagulable by Heat in Neutral Solution.**—The filtrate is then neutralised with potassium hydroxide, using phenolphthalein as indicator, and heated to boiling. The nitrogen in the precipitate (which rarely forms) represents the coagulable proteids. **Estimation of Nitrogen in the Form of Caseoses (Albumoses).**—The filtrate is treated with 1 c.c. of 50 per cent. sulphuric acid, saturated with zinc sulphate, and heated at 70°. When cold, the precipitate is washed with a slightly acid saturated solution of zinc sulphate. The nitrogen contained in this precipitate represents the albumoses. **Estimation of Nitrogen in the Form of Peptones.**—One hundred c.c. of the aqueous extract are put into a 250 c.c. flask, 100 c.c. of water are added, and 5 c.c. of sulphuric acid. A 30 per cent. solution of phosphotungstic acid is then added drop by drop until no further precipitation takes place. After diluting to 250 c.c.

and filtering, 50 or 100 c.c. are used for the estimation of nitrogen, and the peptones are thus found by difference. Other processes are described, such as precipitation by tannic acid and salt, and precipitation by bromine and hydrochloric acid, but these are sometimes less satisfactory. *Estimation of Nitrogen in the Form of Amino-acid Compounds.*—After removal of the peptones, the filtrate contains amino-acids and ammonia. By estimating the total nitrogen in this filtrate and allowing for that present as ammonia, the amino-acids may be calculated. *Estimation of Nitrogen in the Form of Ammonia.*—One hundred c.c. of the filtrate, obtained on precipitating the aqueous solution with salt and tannic acid, are distilled with addition of magnesium oxide, and the ammonia is titrated as usual. *Estimation of Nitrogen in the Form of Unsaturated Paracasein Lactate.*—The mass insoluble in water is repeatedly extracted with a 5 per cent. solution of salt until 500 c.c. are collected, and the nitrogen contained in an aliquot part of the filtrate is then estimated as usual.

The processes recommended for the estimation of the different proteids in milk are similar to those described for cheese. The casein, however, is separated by diluting 10 grams of milk with 90 c.c. of water at 40–42° and adding 1.5 c.c. of 10 per cent. acetic acid. A somewhat brief description is also given of a process for the estimation of chloroform in milk or cheese, as this is said to be used for antiseptic purposes; it is based on the decomposition of chloroform by alcoholic potassium hydroxide at 110°.

L. DE K.

Estimation of Soil Acidity and the Lime Requirements of Soils. F. P. VEITCH (*J. Amer. Chem. Soc.*, 1902, 24, 1120–1128).—The soil (three portions of 10 grams) is treated with water (50–60 c.c.) and standard lime-water (10, 20, and 30 c.c.) and at once evaporated to dryness in platinum dishes. It is then transferred to Jena-glass flasks with 100 c.c. of water, kept over-night, being occasionally shaken, and filtered. The clear or only slightly turbid filtrate (50 c.c.) is boiled in a Jena flask with a few drops of phenolphthalein solution until it becomes pink, or until the volume is reduced to about 5 c.c., if no colour is produced. Then, with the two portions of treated soil, one of which has been made alkaline and the other of which is still acid, as guides, three fresh portions of 10 grams are prepared, with addition of lime-water as before, except that the amounts of lime-water differ by only 1–2 c.c. The process already described is repeated, the smallest amount of lime-water which produces the pink colour being taken as the acidity equivalent of the soil.

A number of results obtained by the method are given, as well as the indicated lime requirements of the various soils.

N. H. J. M.

General and Physical Chemistry.

Optical Rotating Power of Camphor. HERMAN SCHLUNDT (*J. Physical Chem.*, 1903, 7, 194—206).—The rotation of camphor was determined at various concentrations and temperatures in carbon disulphide, sulphur monochloride, phosphorus trichloride, and sulphur dioxide. It was found that the specific rotation increased with concentration and with temperature. The following values were obtained:

Solvent.	<i>t.</i>	$[\alpha]_D$.
Carbon disulphide.....	20°	55·41
Sulphur dioxide.....	20	55·64
Phosphorus trichloride	20	54·8
" " 	0	53·1
" " 	40	56·4

With sulphur monochloride solutions, ordinary gas light was employed; the specific rotation at 20° varied from 37·3 to 42·4 for 3·4 to 20·2 per cent. solutions. L. M. J.

Law of Substitution in Aromatic Compounds. HUGO KAUFFMANN (*J. pr. Chem.*, 1903, [ii], 67, 334—338. Compare Abstr., 1900, i, 480; 1901, i, 318; and Flürscheim, Abstr., 1903, i, 79).—The following table shows the extent to which the molecular magnetic rotations of a number of benzene derivatives vary from the normal, the abnormality of benzene being taken as ± 0 :

Dimethyl- <i>p</i> -phenylenedi- amine	10·967	Diphenyl	1·622
Diethylaniline	8·816	Catechol	1·350
Dimethylaniline	8·587	Pyrogallol	1·163
Dimethyl- <i>p</i> -toluidine ...	7·518	Phenol	0·662
<i>o</i> -Phenylenediamine.....	6·165	Ethylbenzene	0·084
<i>m</i> -Phenylenediamine ...	5·617	Benzene	$\pm 0\ 000$
<i>o</i> -Anisidine	5·250	Bromobenzene.....	—0·086
<i>p</i> -Anisidine	4·834	Benzaldehyde	—0·196
<i>o</i> -Toluidine	3·922	Benzonitrile	—0·201
Aniline.....	3·821	Ethyl benzoate	—0·382
<i>p</i> -Toluidine	3·069	Acetophenone	—0·560
Quinol dimethyl ether...	2·999	Benzoyl chloride	—1·116
<i>m</i> -Toluidine	2·932	<i>o</i> -Nitrotoluene	—1·730
Acetanilide	1·949	Nitrobenzene	—2·152
		<i>p</i> -Nitrotoluene	—2·321

Those derivatives which have an abnormality greater than +1 are rendered luminous by Tesla-rays, the intensity of illumination increasing with the abnormality. Those compounds with a *plus* abnormality

and also bromobenzene, can be substituted in the *ortho*- and *para*-positions, the others in the *meta*-position. The higher the abnormality, the greater the ease with which substitution takes place.

Salt formation decreases the abnormality of the amines, but increases that of the phenols. This explains the formation of *meta*-substituted compounds from aniline sulphate, the stability of the salts of unstable bases, and the oxidation by air of phenols in alkaline solution.

G. Y.

Radiation from Polonium and the Secondary Radiation which it Produces. HENRI BECQUEREL (*Compt. rend.*, 1903, 136, 977—982).—An account of the impressions made on a photographic plate by metallic polonium. The polonium emits rays which, when they emerge from material which they have penetrated, set up a secondary radiation. The α -rays from polonium are very penetrating. Of the three distinct parts which constitute the radiation from radium, two are present in the polonium radiation, and it has not been possible to identify anything of the nature of cathode rays in this. The radiation from uranium (*Abstr.*, 1902, ii, 238) consists solely of rays, analogous to the α -rays of radium and polonium, which are deviable by a magnetic field. In the uranium rays, no canal rays or cathode rays are to be found.

It is pointed out that the designation *α -rays*, given by Rutherford to the absorbable part of the uranium radiation, is apt to lead to confusion.

J. McC.

Radioactive Lead as a Primary Active Substance. KARL A. HOFMANN and V. WÖFLI (*Ber.*, 1903, 36, 1040—1047. Compare *Abstr.*, 1901, ii, 19, 159, 385, 655; 1902, ii, 78, 261, 397).—A metal has been isolated from pitchblende, the salts of which resemble, in all chemical characters, those of lead. These preparations exhibit in very high degree both α - and β -radioactivity, the former variety being easily absorbable, and the latter having greater permeating power. The α -activity is communicated to metals, platinum, gold, lead, and more especially palladium, which are immersed in solutions of this radioactive lead, these metals acquiring the property in a greater degree than the original preparation. The metals retain this induced radioactivity after washing or drying for many months, but lose it in a few minutes on heating. In this treatment with metals, the active preparation of lead loses its α -activity, but regains it entirely on keeping for a few weeks.

The β -activity can only be communicated by very intimately mixing the radioactive preparation with the foreign substance, for example, by dissolving both materials in the same solution. The β -activity is not removed by heating to redness. On subjecting lead to the influence of a polonium preparation which was powerfully exhibiting α -radioactivity, no β -activity was acquired by the lead; it merely possessed induced α -activity.

K. J. P. O.

Action of Radioactive Substances on the Electrical Conductivity of Selenium. EDMOND VAN AUBEL (*Compt. rend.*, 1903, 136, 929—930).—The electrical resistance of a piece of selenium was determined by the Wheatstone bridge method to be 496,000 ohms. It was then exposed at a distance of about 3 cm. from the surface of hydrogen peroxide for three or four minutes, and the resistance decreased to 324,000 ohms. When similarly exposed for fifteen minutes to turpentine, the resistance diminished from 461,000 ohms. to 386,000 ohms. As light, radium rays, and Röntgen rays produce a similar diminution of the resistance of selenium, the experiments seem to show that hydrogen peroxide and turpentine emit rays.

J. McC.

Resistance of the Ions and the Mechanical Friction of the Solvent. FRIEDRICH KOHLRAUSCH (*Proc. Roy. Soc.*, 1903, 71, 338—350).—The conductivity of dilute solutions may be expressed by the formula: $\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + \beta(t - 18)^2]$, the values for the constant differing little for $N/10000$ and $N/1000$ solutions. By extrapolating the curves, it is found they all pass through zero value between -35° and -41° . As a first approximation, this temperature may be assumed constant, and hence $\beta = C(\alpha - A)$, where C and A are constants common to all electrolytes and the common point is at the value $-1/C$. Introducing this value t_0 where the conductivity is zero, the conductivity of all electrolytes is given by the formula $\kappa_t = P(t - t_0) + Q(t - t_0)^2$, where P and Q are specific constants. If the curve representing the fluidity of water (with arbitrary factor) be drawn on the same chart as the conductivity curves, it is seen to be closely analogous, and it passes through the zero value at -34° , so that the temperature change and zero value of the fluidity are approximately equal to those of the conductivity. [It is important to emphasise the fact that it is not supposed that the values for either constant would really become zero at this temperature, as a new expression would be required before the zero value was actually reached, as in the gas equation $PV = RT$.] The author hence considers that the electrolytic resistance must be considered as a resistance of the solvent, and suggests that each ion is enveloped by a water atmosphere of considerable thickness. In the case of a sluggish ion, only the viscosity friction need be considered, and the temperature coefficient of the resistance is equal to that of the viscosity. The thickness of the water atmosphere, however, varies with the nature of the ions. The hypothesis is not further developed, but the author invites its experimental or theoretical continuation (see Bousfield and Lowry, this vol., ii, 52).

L. M. J.

Conductivity and Internal Friction of Solutions. G. RUDORF (*Zeit. physikal. Chem.*, 1903, 43, 257—304).—In continuation of Wolf's work (*Abstr.*, 1902, ii, 299), the conductivities of solutions of sodium bromide, potassium chloride, and sodium acetate in mixtures of water and acetic acid were determined. The solutions were 0.01, 0.025, and 0.05 N with respect to salt and up to 10 N with respect to acetic acid. If κ is the conductivity of the aqueous solution of the

salt, κ , that of the acid of normality n , and κ_2 that of the mixture, the following relationship, $100[(\kappa + \kappa_1) - \kappa_2]/n\kappa = D = 9.45$, holds for concentrations up to $n = 1$. As the value of n increases, D diminishes in value.

The maximum conductivity of acetic acid solution in water is displaced by the addition of sodium acetate. This is due to the isohydric influence of the added salt, and the maximum disappears entirely when the solution is $0.05N$ with respect to added salt.

The value of D gives a measure of the retarding influence of acetic acid, when regarded as a solvent, on the mobility of the ions. The dissociation isotherm is only applicable for acetic acid up to a concentration of $0.25N$, but if a correction for this D -value be introduced, Ostwald's law may be satisfactorily applied up to the concentration $0.6N$.

The internal friction of various solutions of acetic acid, sugar, tartaric acid, *n*-propyl alcohol, isopropyl alcohol, carbamide, and acetone have been determined at 25° by the Poiseuille and Ostwald method. Solutions of sodium bromide, carbamide, and quinol in mixtures of water and acetic acid were also examined. Arrhenius's exponential formula, $\eta = A^n$, is not in accord with the results obtained, nor is the linear formula, $\eta = 1 + an$. No connection between the D -value and the internal friction could be established. It seems probable that if at all concentrations the same molecular species were present in the solution, the linear formula would be applicable. This seems never to be the case, and the deviation is caused either by polymerisation or by the formation of loose compounds between the solvent and the dissolved substance. When the deviation is due to polymerisation, it is proportional to the normality of the solution, but when due to the formation of loose compounds it is proportional to the square of the normality. A very decided parallelism exists between the curves of internal friction and those of depression of freezing point for non-electrolytes. For electrolytes, the electro-striction causes a complication.

Carbamide in small quantity produces a lowering of the internal friction of water; this is, in all probability, not due to hydrolysis.

J. McC.

Relations between the Nature and Properties of Solvents and their Ionising Capacity. Electrical Conductivity and its Temperature Coefficients in Organic Solvents. GIULIO COFFETTI (*Gazzetta*, 1903, 33, i, 53—68).—The author has determined the electrical conductivities at various temperatures of solutions of lithium chloride, sodium iodide, cadmium iodide and chloride in methyl alcohol, sodium chloride, bromide and iodide in amyl alcohol, lithium and hydrogen chlorides in acetaldehyde and paracetaldehyde, lithium chloride, sodium and cadmium iodides in acetone, lithium chloride and sodium and cadmium iodides in propionitrile, and lithium and cadmium iodides in nitromethane, the results being as follows.

The temperature coefficient of conductivity varies both with the solvent and with the solute. For solutions of the strong electrolytes, it is independent of the dilution, and changes but little when the sol-

vent is changed, the values lying mostly between 0.012 and 0.014. With weak electrolytes, on the other hand, the temperature coefficient of conductivity generally increases with the dilution. Solutions of lithium chloride in acetaldehyde or paracetaldehyde and of cadmium iodide in propionitrile have negative temperature coefficients. Acetaldehyde seems to have a greater dissociating power than paracetaldehyde, so that the association of a solvent cannot be regarded as the cause of its dissociating property. Hydrogen chloride has a very low conductivity in acetaldehyde or paracetaldehyde, probably on account of combination taking place between the solvent and solute. Nitromethane has a very high dielectric constant (56.36 at 15°), and, as Nernst's theory predicts, a strong electrolyte, such as lithium iodide, is very strongly dissociated in this solvent. T. H. P.

Electrical Conductivity of Solutions at the Freezing Point of Water. W. C. DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1903, 71, 332—338).—The chief results obtained are summarised in the following table, in which m = number of gram-equivalents of solute per thousand grams of solution, whilst the numbers given for each salt are the ratios of the equivalent conductivity to that at infinite dilution :

m .	KCl.	$\frac{1}{2}$ BaCl ₂ .	$\frac{1}{2}$ K ₂ Cr ₂ O ₇ .	$\frac{1}{2}$ CuSO ₄ .	$\frac{1}{2}$ MgSO ₄ .
0.00001	1.000	1.000	0.991	0.998	0.983
0.0001	0.999	0.995	0.929	0.967	0.950
0.001	0.992	0.969	0.870	0.863	0.864
0.01	0.962	0.896	0.858	0.638	0.659
0.10	0.896	0.778	0.783	0.405	0.435
1.0	0.856	0.665	—	0.230	0.264
2.0	—	0.632	—	0.194	0.192

L. M. J.

Conductive Power of Hydrazine and of Substances Dissolved therein. ERNST COHEN and CORNELIS A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 551—556).—The properties of hydrazine lead to the conclusion that it might be an ionising solvent. Its dielectric constant, determined by Drude, is 53 at 22°. The lowest conductivity for the pure substance, prepared from hydrazine hydrate and barium oxide (*Abstr.*, 1897, ii, 22), was 4×10^{-5} at 25°. The conductivity was determined in a specially-constructed cell. Solutions of potassium chloride, bromide, and iodide were examined. On account of the difficulty of determining the concentration, since but little hydrazine was available, the results cannot be assumed to be accurate, but they show that as an ionising solvent, hydrazine is comparable with water.

The addition of ammonia to hydrazine only slightly increases the conductivity. When water is added to hydrazine, the conductivity falls to a minimum, reached when the mixture contains 60 mols. of water to 100 mols. of hydrazine. J. McC.

Behaviour of Diaphragms in the Electrolysis of Salt Solutions. II. WILHELM HITTOFF (*Zeit. physikal. Chem.*, 1903, 43, 239—249).—Some corrections of numerical errors in the first paper and further examples of the anomalous results obtained by electrolysis through animal membranes are given. The author considers the decrease in the transport number of the anion with dilution, in the case of cadmium salts, to be due to the formation of complex molecules which are decomposed by dilution. The transport number was found to decrease from 0.844 for a solution of 1 part of cadmium chloride in 1.858 of water, to 0.636 for a solution of 1 in 414.15 parts. Results were obtained with goldbeaters' skin membranes similar to those previously recorded, the solution being separated into concentrated and dilute portions. The author does not consider the results are satisfactorily explained by the existing theories (see *Abstr.*, 1902, ii, 59). L. M. J.

Electrolysis of Water. WILLIS R. WHITNEY (*J. Physical Chem.*, 1903, 7, 190—193).—The electrolysis of water at low voltages is capable of explanation without any additions to the usually accepted theory. In the case of an aqueous solution, the electrodes at an electromotive force of 1 volt become so charged with oxygen and hydrogen that they are to be considered as gas electrodes of low concentration. The gases dissolve in the water and tend to reach a saturation corresponding with the above concentration, but in an open vessel this would probably never be attained. L. M. J.

Ozone as an Oxidation Agent. ROBERT LUTHER and J. K. H. INGLIS (*Zeit. physikal. Chem.*, 1903, 43, 203—238).—The anode liquid of an electrolytic cell contains a strong oxidiser, and a platinum electrode in it combined with a calomel electrode yields an *E.M.F.* of about 1.1 volts. The authors consider this oxidiser to be most probably ozone, and the paper contains investigations on the behaviour of ozone electrodes. It is shown that different electrodes in different acids saturated with ozone give, within narrow limits, the same *E.M.F.* against a calomel electrode. Electrodes charged with oxygen yield a somewhat lower value, whilst a hydrogen charge raises the oxidation potential; the latter increase, however, soon passes away, the electrode regaining its normal value. It was found that the electrode could be rendered free from either oxygen or hydrogen by a mixture of ferrous and ferric salts. The authors, from these facts, consider that oxygen is a primary product of the electrolytic reduction of ozone. To determine the equation representing this electrolytic reduction, experiments were made on the effect of changes of concentration of ozone and hydrogen on the *E.M.F.* It was found that the potential was given by the equation $\pi_{\text{ozone}} - \pi_{\text{sol.}} = \pi_0 + RT/F \cdot \log C_{\text{ozone}} \times C_{\text{H}}$, and for an ozone-hydrogen cell, $\pi = 1.861 + 0.054 \log C_{\text{ozone}}$ volts. The result is not in accord with any of the equations the authors had previously considered probable, and it is suggested that the solution of ozone acts as a weak acid of the composition H_2O_5 or H_2O_7 . In the paper, the authors collect some of the results of the work of Brodie and others on oxidation by ozone, where

it is shown that in acid solution, ozone liberates from potassium iodide three equivalents of iodine, whilst in neutral solution only two are liberated.

L. M. J.

The Decomposition Curves of Solutions of Copper Salts.
 EMIL ABEL (*Zeit. Elektrochem.*, 1903, 9, 268—269).—Heiberg (this vol., ii, 263) explains the rise in the decomposition curve of copper sulphate which begins about 0.1 volt before the decomposition point of copper sulphate by assuming the discharge of Cu^+ ions to metallic copper. The discharge potential of cuprous ions is higher than that of the cupric ions when the concentration of the cuprous ions is smaller than that corresponding with equilibrium between the two kinds of ions, hence it is necessary to suppose all the solutions were supersaturated with cuprous ions. This is avoided by supposing that the decomposition point observed is due to the change $\text{Cu}^{++} = \text{Cu}^+ + F$. This takes place at a lower potential than the discharge of cupric ions when the solution is not saturated with cuprous ions.

T. E.

Electrolytic Solution of Platinum by Alternating Currents.
 RUDOLF RUER (*Zeit. Elektrochem.*, 1903, 9, 235—239).—Platinum electrodes, *A*, *B*, and *C*, immersed in sulphuric acid, are so connected that an alternating current may be passed between *A* and *B*, and, simultaneously, a direct current between *C* and *A* and *B* together, the two latter acting as anode. It is found that the platinum is not dissolved by the alternating current alone, but when the electrodes between which the alternating current is passing are submitted to anodic polarisation, the platinum is dissolved.

The addition of an oxidising agent (even atmospheric oxygen) to the sulphuric acid has the same effect. The maximum rate of dissolution is obtained when the strength of the alternating current is in a definite ratio to the strength of the polarising current or to the concentration of the dissolved oxidising agent.

Most electrolytes behave in the same way as sulphuric acid. In a few (the anions of which have a great tendency to form complex ions with platinum), the alternating current produces solution of platinum, independently of the direct current, but in these cases the direct current alone also dissolves platinum in certain circumstances.

When lead is used as anode in sulphuric acid, it becomes coated with lead peroxide and is but little attacked, but if an alternating current is passed between two such lead anodes, lead sulphate is formed rapidly. The hydrogen evolved during the one period of the alternation obviously reduces the lead peroxide to lead oxide, which is readily acted on by the acid. If it be assumed that a platinum anode is coated with a very thin film of a peroxide, then the action of an alternating current in causing its dissolution is readily explained in the same way, especially the curious fact that a small alternating current produces no dissolution when a strong polarising current or a strong oxidising agent is used, because in these circumstances the weak (alternating) cathodic polarisation would be insufficient to reduce the peroxide. That a very strong alternating current produces a decreased amount of dissolution is also explained, because then the peroxide would be

reduced to metallic platinum, which is also insoluble, and the electrode would be simply disintegrated, which is the case. Passive iron behaves like platinum towards alternating currents. T. E.

Abnormal Electrolytes. PAUL WALDEN (*Zeit. physikal. Chem.*, 1903, 43, 385—464).—The paper contains a review of recent work dealing with the conductivity of solutions in cases where the solvent is other than water, and the solute is a substance not generally regarded as an electrolyte. Besides this general matter, a large number of experimental data are given in the paper, some of which have been already published and discussed (compare Walden, Abstr., 1901, ii, 11; Walden and Centnerszwer, Abstr., 1902, ii, 245; Walden, Abstr., 1902, i, 169, 536, 554).

Further experiments are recorded in which solutions of bromine in liquid sulphur dioxide and of iodine in sulphuryl chloride (below 0°) were found to have an appreciable conductivity; the same holds for solutions of iodine chloride, iodine trichloride, and iodine bromide in liquid sulphur dioxide, arsenious chloride, or sulphuryl chloride. In all these cases, the equivalent conductivity is greater the lower the temperature, and its value increases with the dilution. The author, by way of explanation, adopts the view that bromine and iodine may exist not only as anions, but also as cations: Br^+ , I^+ , I^{++} .

The author has studied also the conductivity of phosphorus tribromide and pentabromide, arsenious bromide, antimony pentachloride, stannic chloride and bromide, and sulphur bromide in liquid sulphur dioxide, and of phosphorus pentabromide and stannic iodide in arsenious chloride, and concludes that the assumption of the following cations is necessary: P^{+++} , P^{++++} , As^{+++} , Sb^{+++} , Sb^{++++} , Sn^{++++} , and S_2^{++} .

From investigation of solutions of quinoline, pyridine, and α -picoline in sulphur dioxide and of quinoline in arsenious chloride, sulphuryl chloride, and phosphorus oxychloride, it appears that tertiary nitrogen bases yield divalent cations $(\text{RN})^{++}$.

From the behaviour of triphenylcarbinol, trimethylcarbinol, triphenylmethyl (also its chloride, bromide, and iodide), and trimethylcarbinyl iodide, the existence of the cations $(\text{C}_6\text{H}_5)_3\text{C}^+$ and $(\text{CH}_3)_3\text{C}^+$ is deduced. The number of the radicles attached to the central carbon atom appears to determine the tendency to dissociation, for the tertiary halogen compounds dissociate more readily than the secondary, and still more so than the primary, halogen compounds. The phenyl radicle especially has the power to produce carbonium bases and salts that are capable of dissociation.

Experiments with bromoacetyl bromide and α -bromoisobutyryl bromide in sulphur dioxide solution make it probable that there exist acid cations of the type $(\text{R}\cdot\text{CO})^+$, where R is an organic radicle. Similarly, experiments with solutions of phosphorus oxychloride in liquid sulphur dioxide point to the existence of the cation PO^{+++} .

J. C. P.

Magnetic and Electric Dichroism of Liquids. GEORGES MESLIN (*Compt. rend.*, 1903, 136, 888—889, 930—932).—When a suspension of potassium dichromate in carbon disulphide or turpentine is placed

in a strong magnetic field, it becomes dichroic. Carbon disulphide, turpentine, or an aqueous solution of potassium dichromate do not exhibit the phenomenon. The dichroism can also be produced with other liquids, such as benzene or stannous chloride, and with various coloured substances, such as methyl-orange, eosin, &c. The dichroism, which may be either positive or negative, depends on the nature of both the solvent and the dissolved substance. In carbon disulphide, cupric sulphate exhibits positive dichroism, whilst in turpentine it shows negative dichroism.

When a ray of polarised light is passed through the dichroic solutions, the plane of polarisation is rotated, but no elliptical polarisation or magnetic double refraction could be found. The asymmetry caused by the magnetic field persists for some seconds after the field has been cut off, but disappears more rapidly if the liquid is shaken.

The only case of dichroism produced by an electric field was that found for a solution of methyl-orange in carbon disulphide; in the electric field, this solution is negatively dichroic, whilst in the magnetic field it is positively dichroic.

J. McC.

Apparatus for Measuring the Expansion of Gases with Temperature under Constant Pressure. THEODORE W. RICHARDS and KENNETH LAMARTINE MARK (*Zeit. physikal. Chem.*, 1903, 43, 475—486).—In the apparatus described, provision is made for keeping the whole of the gas under observation at the same temperature, and the pressure is measured to within 0.01 mm. of mercury with the aid of Rayleigh's barometer (see Abstr., 1893, ii, 514). The temperature interval, further, for which the expansion has been measured is small, namely, from 0° to 32.38°, the transition temperature of sodium sulphate.

The coefficients of expansion thus obtained are as follows: hydrogen, 0.003659; nitrogen containing 2 per cent. of hydrogen, 0.003660; carbon dioxide, 0.003727.

J. C. P.

Specific Heats and Heats of Vaporisation or Fusion of Aniline and other Organic Compounds. ROBERT DE FORCRAND (*Compt. rend.*, 1903, 136, 945—948. Compare Abstr., 1901, ii, 372, 594, 641; 1902, ii, 379; this vol., ii, 267, 353).—The author has verified the relationship $(L + S)/T = 30$ (*loc. cit.*) for aniline, benzene, nitrobenzene, and acetic acid. The results in all cases appear to give low values, but this is attributed to the fact that the specific heat of the solid has not been exactly determined on account of part of the substance remaining in a superfused condition. The specific heat of solid aniline is shown to be 0.2230 at -15°, and its molecular heat of fusion is 3.711 Cal. The molecular heat of fusion of acetic acid is 2.629 Cal. With these new numbers, values are obtained which confirm the above relationship.

J. McC.

Relationship between Heat of Vaporisation and Critical Magnitudes. A. J. BATSCHINSKI (*Zeit. physikal. Chem.*, 1903, 43, 369—371).—The connection between the heat of vaporisation, r , and the critical values, T_k and v_k , is better represented by the

formula $Mr = 2T + 6.5(T_k^2/T)\{1/[(v/v_k) + 0.44]\}$ than by the formula given by Bakker (*ibid.*, 1895, 18, 519). It is shown that for ether and chloroform this formula gives good results. The formula is only applicable to non-associated substances, and may in such cases be employed for determining the critical temperature. J. McC.

Critical Phenomena of Partially Miscible Liquids. Ethane and Methyl Alcohol. JOHAN P. KUENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 473—482).—The critical curves of partially miscible liquids are discussed (compare Kuenen and Robson, *Abstr.*, 1899, ii, 356, and van der Waals, *Abstr.*, 1900, ii, 134). The author arrives at the conclusion that when the three phase pressure lies between the vapour pressures of the components, the critical curve is concave towards the temperature-axis, and when it is higher than the vapour pressures of the components the curve is convex (as in the case of ether and water). The effect of molecular association on the critical temperature is also considered.

The critical curve for mixtures of ethane and methyl alcohol rises normally from the critical point of methyl alcohol and passes through a maximum at 120°. It falls to a minimum between 25° and 30°, then rises rapidly.

Down to -78°, ethyl alcohol and ethane remain miscible in all proportions. J. McC.

F. W. Clarke's "New Thermochemical Law." JULIUS THOMSEN (*Zeit. physikal. Chem.*, 1903, 43, 487—493).—The above-mentioned empirical law, according to which the heats of combustion of organic compounds are multiples of the same constant, is discussed by the author. He finds serious differences between calculated and experimental values, and declares that the law is of no value.

J. C. P.

Heats of Formation of Barium Compounds. ANTOINE GUNTZ (*Compt. rend.*, 1903, 136, 1071—1072).—The author has determined indirectly the heats of formation of the following barium compounds. Barium monoxide, 133.4 Cal. Barium nitride, Ba_3N_2 , 149.4 Cal. Barium hydride, 37.5 Cal. Barium ammonium, $Ba(NH_2)_2$, 53.3 Cal.

T. A. H.

Heats of Combustion of Organic Compounds viewed as Additive Properties. Hydrocarbons. PAUL LEMOULT (*Compt. rend.*, 1903, 136, 895—898).—For hydrocarbons of the paraffin series, the molecular heat of combustion is given by $(157n + 55)$ Cal., where n is the number of carbon atoms present in the molecule. For hydrocarbons of the olefine series, the value is $(157n + 28)$ Cal., and for those of the acetylene series it is $(157n + 2)$ Cal.

In the case of aromatic hydrocarbons, the value is $(115.75n + 82.5)$ Cal., and the value may also be calculated for mixed hydrocarbons, as well as for alicyclic hydrocarbons. J. McC.

Redetermination of the Transition Temperature of Sodium Sulphate, referred to the International Scale. THEODORE W. RICHARDS and ROGER CLARK WELLS (*Zeit. physikal. Chem.*, 1903, 43, 465—474. Compare Richards and Churchill, *Abstr.*, 1898, ii, 555).—More exact determination of the transition temperature of sodium sulphate with the aid of various standard thermometers gives the value $32.383^{\circ} \pm 0.001^{\circ}$ (on the hydrogen scale). The authors consider that this temperature is quite as steady and defined as either of the two fixed points commonly used in thermometric work, and its use is accordingly recommended. J. C. P.

Molecular Rise of Boiling Point for Nitrobenzene. HEINRICH BILTZ (*Ber.*, 1903, 36, 1110).—Bachmann and Dziewoński (this vol., ii, 354) found the constant for the molecular rise of boiling point of nitrobenzene to be 50.1° , a value varying from that obtained by the author in 1895 (*Abstr.*, 1896, ii, 412), namely, 46° . The author has since redetermined the constant and has found it to be 50.4° (*Monatsh.*, 1901, 22, 627). A. McK.

Modification of the Landsberger Apparatus for Molecular Weight Determination. ALFRED LEHNER (*Ber.*, 1903, 36, 1105—1110).—A sketch of the apparatus and a description of the method are given. The advantage, as compared with the apparatus of Landsberger and the modifications of it by McCoy and Smits, is that the quantity of solvents required is very small. Determinations can be quickly made, since it is possible to add the weighed quantity of substance directly after the boiling point of the solvent has been taken, and to proceed at once to determine the rise of the boiling point. A. McK.

Determination of Molecular Weights. HENRY C. BIDDLE (*Amer. Chem. J.*, 1903, 29, 341—352).—A method is described by which the difference between the vapour pressures of a solution and the solvent can be measured directly. The apparatus consists of a differential manometer, in which olive oil is used, and two flasks of nearly the same capacity (about 250 c.c.); the flasks are connected with the manometer by capillary tubes, which are of equal length and form one piece with the ground-glass stoppers of the flasks. A tube provided with a glass stop-cock passes through the stopper of each flask and extends to 1—2 cm. from the bottom; the part of each tube above the stop-cock is graduated and has a capacity of 10—15 c.c. By means of a T-piece attached to that portion of the capillary tube which connects the stoppers of the flasks, the whole apparatus can be readily exhausted. A complete description and diagram of this apparatus are given in the original paper. In making a determination, the flasks are maintained at a constant temperature by means of a thermostat. The pressure within the apparatus is reduced to about 300 mm. of mercury, equal volumes (10—15 c.c.) of solution and solvent respectively are introduced into the flasks, and the difference

between the vapour pressures is registered by the manometer. The molecular weight is calculated from the equation

$$M = K \{100/(f-f')\} \cdot (P/W),$$

where K is the diminution in the vapour pressure produced when a gram-molecular weight of the substance is dissolved in 100 grams of the solvent, and P and W denote the weight in grams of the substance and solvent respectively.

By this method, the molecular weights of naphthalene, cinnamic acid, salicylic acid, and iodine in ethereal solution, and of naphthalene, phenanthrene, sulphur, phosphorus, and iodine in carbon disulphide solution were determined. In the case of iodine, it was found that in each solution the molecule is diatomic. In order to ascertain the molecular complexity of iodine in alcoholic solution, the osmotic pressure was determined, the vapour pressure of alcohol being insufficient to afford trustworthy data by the method just described. The results point conclusively to the diatomic condition of iodine in alcoholic solution, and confirm the ebullioscopic determinations of Beckmann and Stock (*Abstr.*, 1895, ii, 382).

E. G.

Freezing Point Depression in Electrolytic Solutions. JAMES WALKER and A. J. ROBERTSON (*Proc. Roy. Soc. Edin.*, 1903, 24, 363—379).—Freezing point depressions and ionisation coefficients were determined by a method in which the systematic errors introduced differ from those introduced in the ordinary methods. The freezing point was obtained by the addition of excess of ice to the solution, and when a constant value had been reached some of the liquid was filtered off and analysed. To obtain the ionisation value, two experiments were made in succession, one with the electrolyte desired, the second with a non-electrolyte, or more conveniently with a slightly dissociated compound of known ionisation. The availability of the method is clearly shown by experiments with malonic and acetic acids, and the agreement of the results for strong electrolytes with those of other observers is seen from the following table of equivalent depressions in 0.05 N solution:

	HCl.	KCl.	NaCl.
Loomis.....	3.59	3.50	3.531
Barnes.....	3.597	3.504	3.536
Walker & Robertson	3.590	3.493	3.526

L. M. J.

The Variability of the Quantity b of the Equation of Condition. JOHANNES D. VAN DER WAALS, *jud.* (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 487—497).—In order to make a correction for the space actually occupied by the molecules of a gas, van der Waals (*sen.*) has deduced the term $17b^2/32V$, whilst Boltzmann has deduced $3b^2/8V$ to be introduced into the equation of condition. The author deduces mathematically that there is no justification of the former term, and gives a shorter process for deducing that of Boltzmann.

J. McC.

Idea of Independent Components. RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1903, 43, 376. Compare this vol., ii, 356).—The definition of independent components given by the author places no restriction on the application of the phase rule, but that given by Nernst (this vol., ii, 356) requires in certain cases a limitation of the phase rule.

J. McC.

Equilibrium in the System Composed of Sodium Carbonate, Sodium Hydrogen Carbonate, Carbon Dioxide, and Water. HERBERT N. MCCOY (*Amer. Chem. J.*, 1903, 29, 437—462).—The source of error in many solubility determinations of hydrogen carbonates is due to the loss of carbon dioxide, sodium hydrogen carbonate, for example, being hydrolytically dissociated according to the equation $\text{NaHCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{H}_2\text{CO}_3$. When a solution of sodium hydrogen carbonate of known strength is taken, it is not possible to measure the amount of hydrolytic dissociation by determining the concentration of the vapour phase, since sodium hydrogen carbonate is itself an acid and can act on sodium hydroxide thus: $\text{NaHCO}_3 + \text{NaOH} \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$. The equilibrium between sodium carbonate, sodium hydrogen carbonate, carbon dioxide, and water was experimentally determined by the author by an examination of the liquid and vapour phases in equilibrium with one another at 25°. The equilibrium is expressed by $2x^2C/kP(1-x) = K$, where x is the fraction of sodium in the form of hydrogen carbonate, $1-x$ the fraction in the form of carbonate, C the concentration of the sodium in gram-atoms per litre, k the solubility coefficient of carbon dioxide in water at 25°, and P the partial pressure of the carbon dioxide. For dilute solutions, $K = 53 \times 10^2$.

From the ionisation constant of carbonic acid, Walker (Abstr., 1900, ii, 268; compare also Walker and Cormack, *Trans.*, 1900, 77, 5) has calculated the hydrolytic dissociation of an $N/10$ solution of sodium hydrogen carbonate. Since, however, sodium hydrogen carbonate is itself a weak acid, the amount of free hydroxide is less than that found by Walker.

The hydrolytic dissociation of sodium carbonate was calculated. In a solution containing 0.5 gram-mol. of sodium carbonate in 10 litres, 6.2 per cent. of the carbonate exists as hydroxide and hydrogen carbonate. The ionisation constant of sodium hydrogen carbonate is nearly equal to the constant of the second hydron of carbonic acid, which is 6.0×10^{-11} , a value $1/5040$ as great as that of the first hydron. When sodium hydrogen carbonate solutions are left exposed to air, they lose carbon dioxide; the state of equilibrium may be calculated when the concentration of the solution and the quantity of carbon dioxide in the air are known.

A. McK.

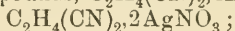
Reduction of some Metallic Haloids by Hydrogen. Influence of Pressure. A. JOUNIAUX (*Compt. rend.*, 1903, 136, 1003—1005).—Certain metals are able to decompose the halogen acids, but an equilibrium becomes established when a certain amount of hydrogen is present, since the reaction is reversible. Several metal haloids

were heated in sealed tubes with hydrogen, and after quickly cooling the concentration of hydrogen and halogen acid in the gas phase was determined. Denoting the ratio of halogen acid to total quantity of gas by α , it is shown that $\log[(2 - \alpha)(1 - \alpha)]/\alpha^2 = m/T + (n + 1)\log T + p + \log 2 + \log \pi/\theta$, where T is the absolute temperature, π the initial pressure of the hydrogen, and θ its temperature (absolute), and m , n , and p are constants. The values of α obtained with silver chloride at 540° and 640° , and with silver bromide at 600° , 655° , and 700° , agree well with those calculated from the formula. Silver iodide and lead iodide are not acted on by hydrogen, and lead chloride and bromide are decomposed to such a small extent that it would be useless to apply the formula. J. McC.

Physical and Natural Equilibrium between the Modifications of Acetaldehyde. I. REINHARD HOLLMANN (*Zeit. physikal. Chem.*, 1903, 43, 129—159).—The most important results have been previously published by Roozeboom (this vol., ii, 135), but the numerical values differ slightly. The natural melting point is 6.75° with 88.3 mol. per cent. paracetaldehyde, the natural boiling point is 41.6° with 53.4 mol. per cent. paracetaldehyde, whilst the natural critical temperature is 218° with 11 mol. per cent. paracetaldehyde. It is seen that at temperatures above about 100° the polymerisation of the saturated vapour increases with temperature. This, although the reverse of previously studied examples of polymerisation, is not contrary to theory. Some preliminary experiments were made with metacetaldehyde which point to the existence of a triple point at 167° , but the investigations are not completed.

L. M. J.

Equilibria in the System: Succinonitrile, Silver Nitrate, Water. W. MIDDELBERG (*Zeit. physikal. Chem.*, 1903, 43, 305—353).—The three binary compounds, $\text{C}_2\text{H}_4(\text{CN})_2, 4\text{AgNO}_3$;



and $\text{C}_2\text{H}_4(\text{CN})_2, \text{AgNO}_3$, can be formed from succinonitrile and silver nitrate. In presence of water, two ternary compounds may be formed; one of these is $2\text{C}_2\text{H}_4(\text{CN})_2, \text{AgNO}_3, \text{H}_2\text{O}$, and the composition of the other is probably to be represented by $4[2\text{C}_2\text{H}_4(\text{CN})_2, \text{AgNO}_3], \text{H}_2\text{O}$.

The equilibrium relationships were determined at the atmospheric pressure.

The binary systems silver nitrate—nitrile, nitrile—water, and silver nitrate—water are discussed. The binary compound, $\text{C}_2\text{H}_4(\text{CN})_2, \text{AgNO}_3$, decomposes at 76.3° into nitrile and the second binary compound, $\text{C}_2\text{H}_4(\text{CN})_2, 2\text{AgNO}_3$. The cryohydric point of a solution of the nitrile in water is -1.2° , and in this system a quadruple point also occurs at 18.5° . The ternary systems are discussed and the results are graphically represented on a triangular diagram. The ternary compound, $2\text{C}_2\text{H}_4(\text{CN})_2, \text{AgNO}_3, \text{H}_2\text{O}$, decomposes at 31.3° into $\text{C}_2\text{H}_4(\text{CN})_2, \text{AgNO}_3$ and solution of the nitrile.

The equilibria and the isotherms are considered from all points of view, but the conclusions cannot be shortly summarised. J. McC.

Velocity of Transformation of Tribromophenol Bromide into Tetrabromophenol. A. H. J. BELZER (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 556—561).—The velocity of transformation of tribromophenol bromide (Benedikt, *Abstr.*, 1879, 717) into tetrabromophenol by means of sulphuric acid was determined by making an emulsion with chloroform. Tribromophenol bromide can be estimated in presence of tetrabromophenol by ascertaining the quantity of iodine liberated from potassium iodide. The action is a unimolecular one. The influence of the quantity of sulphuric acid is very great, and the catalytic agent appears to be sulphur trioxide.

The temperature coefficient was greatest in those cases where the added sulphuric acid contained excess of sulphur trioxide.

The results may be interpreted either by the formula proposed by Benedikt (*loc. cit.*), or by that suggested by Thiele (*Abstr.*, 1900, i, 288), but Kastle's hypothesis (*Abstr.*, 1902, i, 211) of the intermediate formation and decomposition of non-isolated products is not supported.
J. McC.

Catalytic Decomposition of Hydrogen Peroxide and the Mechanism of Induced Oxidations; Nature and Function of Catalase. A. S. LOEVENHART and J. H. KASTLE (*Amer. Chem. J.*, 1903, 29, 397—437).—Bredig and his pupils have found that the catalytic decomposition of hydrogen peroxide by colloidal platinum conforms to the logarithmic equation for reactions of the first order, and conclude that the reaction is represented by the equation $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$ and not by $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. The authors do not accept this conclusion. Bredig has further expressed the analogy between enzymes and colloidal metals by terming the latter "inorganic ferments," and has pointed out the poisonous effect produced by the inhibitory action of many substances on the decomposition of hydrogen peroxide by colloidal gold and platinum. The authors have extended Bredig's work by investigating the effect of various inhibitors on the catalytic decomposition by finely divided silver, platinum, copper, iron, silver oxide, thallium, ferrous oxide, copper sulphate, and catalase, whilst the inhibitors used were hydrocyanic acid, sodium nitrate, potassium nitrate, sodium chloride, sodium fluoride, sodium sulphate, sodium phosphate, sodium hydrogen carbonate, potassium bromide, potassium oxalate, ammonium nitrate, ammonium chloride, ammonium thiocyanate, thiocarbamide, carbamide, hydrogen sulphide, hydroxylamine, phenylhydrazine, acetic acid, and sodium thiosulphate. Some of the inhibitors retard and others accelerate the decomposition of hydrogen peroxide in presence of the various catalysers, a result which in most cases can be explained on purely chemical grounds. In the case of finely divided metals, a thin, insoluble film of a compound of the metal is formed over its surface, and this accounts for the fact that a very small amount of the inhibitor will hold in check a much larger quantity of the metal. The action of silver, for instance, is retarded by sodium chloride, but not by sodium fluoride; in the first place, a coating of silver chloride is produced on the silver; in the second case, there is no such deposition, since silver fluoride is soluble. Certain substances, like ammonium thiocyanate, inhibit because they are themselves

oxidised by the hydrogen peroxide, which is accordingly removed from the solution, and further, because a substance like hydrocyanic acid may be formed in their oxidation. The analogy between the action of inhibitors on the catalytic decomposition by tissue extracts and by colloidal platinum is emphasised by Bredig, but the experiments of the authors indicate that there is no real analogy between inorganic and organic catalysers.

In the absence of formic acid, the oxidation of formaldehyde by hydrogen peroxide is greatly accelerated by finely divided platinum. Although formic acid is about twice as readily oxidised as formaldehyde by hydrogen peroxide in presence of platinum, it was found that, in absence of platinum, formaldehyde was much more readily oxidised by hydrogen peroxide than formic acid. When a mixture of formic acid and formaldehyde in equal amounts is acted on, in presence of spongy platinum, by hydrogen peroxide in quantity sufficient to oxidise either, but not both, to the next higher stage of oxidation, the acid is oxidised almost to the exclusion of the aldehyde. Formic acid is, accordingly, a stronger reducing agent than formaldehyde.

The oxidation of formic acid by hydrogen peroxide in the presence of catalysers was studied. Those substances which effect the decomposition of hydrogen peroxide also accelerate the oxidation. Platinum black and liver catalase do not effect the oxidation of neutral potassium oxalate by hydrogen peroxide.

A. McK.

Colloidal Metals and other Inorganic Colloids. FRIEDRICH BÖCK (*Chem. Centr.*, 1903, i, 614; from *Oesterr. Chem.-Zeit.*, 6, 49—54).—In order to demonstrate experimentally the catalysis of hydrogen peroxide by means of colloidal platinum, its analogy with the process of fermentation, and the "poisoning effect" of hydrocyanic acid on it, six cylindrical gas generating vessels are employed, the delivery tubes of which dip under separate measuring vessels in the same pneumatic trough. Cylinders 1 and 2 are filled with platinum sponge and water, 3 and 4 with colloidal platinum and water, and 5 and 6 with yeast and water. To 2, 4, and 6, a few drops of a very dilute solution of hydrocyanic acid are added, and finally a solution of pure hydrogen peroxide is introduced into each cylinder. Oxygen is evolved from cylinders 1, 3, and 5, but not from 2, 4, and 6.

E. W. W.

An Attempt to Explain Physically the Periodic Regularity of the Chemical Elements. A. J. BATSCINSKI (*Zeit. physikal. Chem.*, 1903, 43, 372—375).—In the periodic recurrence of the properties of the elements with increasing atomic weight, the author sees an analogy with harmonic tones. On this basis, the hypothesis is set up that the atoms are in a state of vibration, and the magnitude of the period of vibration conditions the properties of the elements; the values of the periods of vibration of related elements stand in simple relationship with each other. A harmonic relationship exists between the square root of the atomic weights of many allied elements, thus for fluorine, $\sqrt{m} = 3 \times 1.46$, for chlorine, $\sqrt{m} = 4 \times 1.49$, and for bromine $\sqrt{m} = 6 \times 1.49$.

The author has calculated the square roots of the atomic weights of the elements, and set these in the Mendel'eff table. The table shows a decided tendency to form a harmonic series in the vertical columns, and the deviations are probably to be explained on the ground that the atom is not to be regarded as a material point, but as a material system.

The hypothesis can also be extended to the structure of spectra, and explains why in certain groups of elements the series of spectral lines moves towards the red end with increasing atomic weight.

J. McC.

Inorganic Chemistry.

Synthesis of Water by Combustion. NICOLAE TECLU (*J. pr. Chem.*, 1903, [ii], 67, 426—428).—The author describes a new form of apparatus for the exhibition of the synthesis of water by combustion of hydrogen in air or oxygen. The apparatus may be used also for other syntheses which take place by the combustion of gases.

G. Y.

Existence of Hydrogen Tetroxide. A. M. CLOVER (*Amer. Chem. J.*, 1903, 29, 463—474).—It is supposed by Bach (Abstr., 1900, ii, 470) that when potassium tetroxide is dissolved in dilute acid hydrogen tetroxide is produced. The author has repeated Bach's experimental work, and concludes that there is no evidence for the existence of this substance. The sulphuric acid used was never stronger than $N/1$, an $N/5$ solution being employed in several experiments. The quantity of oxygen evolved was not in excess of that calculated from the equation $5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$, but corresponds with the calculated amount. The requisite amount of acid must, however, be present, but a large excess of acid has no influence on the reaction. Bach obtained an excess of oxygen because he used insufficient acid; manganese dioxide was accordingly deposited, and this decomposed the remaining hydrogen dioxide catalytically. Experiments with commercial sodium dioxide gave similar results.

A. McK.

Action on Metals of Solutions of Hydrochloric Acid in Various Solvents. HARRISON E. PATTEN (*J. Physical Chem.*, 1903, 7, 153—189).—A brief historical review of the action of moisture in causing chemical action is first given, and the author's method of investigating this action is described. The utmost precautions appear to have been taken to ensure the complete absence of moisture, and various samples of each solvent were employed, and frequently slightly different results were obtained with different samples. With a chloroform solution of hydrogen chloride, the electrical conductivity of which was very much less than that of a dry air gap, magnesium and

aluminium showed no evolution of gas, cadmium but very little, whilst zinc was vigorously attacked, more hydrogen being apparently evolved than in a normal hydrogen chloride aqueous solution. After a quantity of zinc had been dissolved, the other metals were corroded owing to the zinc chloride now present in the solution. With carbon tetrachloride as solvent, zinc alone of the above four metals is attacked, but after about an hour it becomes coated with a protective coating, probably zinc chloride. In ethyl chloride solution, zinc is rapidly tarnished with evolution of gas; most of the other metals—for example, silver, copper, manganese, chromium, cobalt, &c.—were tarnished or corroded without evolution of gas, but after standing some hours, gas is evolved by the action of aluminium or magnesium; calcite and witherite were not attacked. In benzene solution, zinc was acted on, hydrogen being evolved with vigour, but aluminium and magnesium were not affected. A trace of water, let in by opening the receiver to the air, did not cause action on the latter metals. Solution of hydrogen chloride in stannic chloride was without action on all the metals and carbonates examined. Its conductivity, however, was considerably greater than that of the benzene or ethyl chloride solutions, both of which have a vigorous action on zinc. Solutions in silicon tetrachloride caused a slight tarnish on copper and lead, but there was no action on other metals and carbonates. A solution in phosphorus trichloride similarly caused merely a slight tarnish on lead, tin, and bismuth. Solution in arsenic trichloride caused evolution of gas in the case of magnesium and zinc, but had no action on carbonates, whilst the solution in antimony chloride had no effect on the metals different from that of the pure solvent alone. Some of the metals act readily on sulphur monochloride; for instance, magnesium, cobalt, copper, antimony, and tellurium; with the other metals, the solution in this solvent caused no evolution of gas, although corrosion or tarnish occurred with zinc, aluminium, cadmium, iron, tin, and bismuth. Solutions in thionyl chloride had but little effect on metals, but vigorously attacked calcite and witherite. The author, in discussing his results, points out that action is not determined by the conductivity, the heat of formation of the chloride, or by the solubility of the chloride in the solvent, but that chemical individuality is apparent. In an addendum, the action of zinc on the benzene solution is treated in further detail, as the author's results are at variance with those of Remsen and Falk, and it is shown that the precautions adopted by the latter to ensure absence of moisture were not as rigorous as his own. L. M. J.

Regularities in the Composition of Halogen Double Salts. FRITZ EPHRAIM (*Ber.*, 1903, 36, 1177—1184).—Mainly a theoretical paper. The author considers that the composition of halogen double salts is dependent on the atomic weight or spatial magnitude of the atoms forming the salt. Thus, vanadium gives the salts $V_2F_6 \cdot 6NH_4F$; $V_2F_6 \cdot 5NaF$; $V_2F_6 \cdot 4KF$, and in these the number of mols. of alkali fluoride present is determined by the magnitude of the alkali metal or radicle. All attempts to prepare the salt $V_2F_6 \cdot 6NaF$ were fruitless; on the other hand, salts containing less alkali fluoride than corresponds with the maximum can be obtained, for example,

$2\text{NH}_4\text{F}, \text{V}_2\text{F}_6$. A similar regularity is seen in the oxyfluorides, $9\text{NH}_4\text{F}, 3\text{VOF}_2$; $8\text{NaF}, 3\text{VOF}_2$; $7\text{KF}, 3\text{VOF}_2$; and in the case of niobium, the salt $3\text{NH}_4\text{F}, \text{NbOF}_3$ is stable, whilst the corresponding potassium salt, on recrystallisation, is converted into the salt $2\text{KF}, \text{NbOF}_3$; the zinc and copper salts are also of the type $\text{ZnF}_2, \text{NbOF}_3$. With tantalum, the salts $3\text{NaF}, \text{TaF}_5$ and $3\text{NH}_4\text{F}, \text{TaF}_5$ are stable, but the potassium salt has the formula $2\text{KF}, \text{TaF}_5$.

With an increase in the atomic weight of the negative metal, a greater stability of the more complex salts is seen; thus, with vanadium (51.2), only the ammonium salt, $3\text{NH}_4\text{F}, \text{VO}_2\text{F}$, is stable, and the corresponding potassium, zinc, and copper salts are not known; but with niobium (93.7) the potassium salt with 3KF can be isolated, but not the corresponding zinc and copper salts.

Similar laws seem to regulate the amount of water of crystallisation contained in the salts, as is seen in the following table:

$\text{CuBr}_2, 2\text{LiBr}, 6\text{H}_2\text{O}$.	$\text{CdBr}_2, \text{NaBr}, 2\frac{1}{2}\text{H}_2\text{O}$.	$\text{SnBr}_4, 2\text{HBr}, 8\text{H}_2\text{O}$.
$\text{CuBr}_2, 2\text{NH}_4\text{Br}, 2\text{H}_2\text{O}$.	$\text{CdBr}_2, \text{KBr}, \frac{1}{2}\text{H}_2\text{O}$.	$\text{SnBr}_4, 2\text{Li}(\text{NH}_4, \text{Na})\text{Br}, 6\text{H}_2\text{O}$.
$\text{CuBr}_2, 2\text{CsBr}, \text{OH}_2\text{O}$.	$\text{CdBr}_2, \text{CsBr}, \text{OH}_2\text{O}$.	$\text{SnBr}_4, 2\text{KBr}, \text{OH}_2\text{O}$.

W. A. D.

Affinity at Low Temperatures. Reactions of Liquid Fluorine at -187° . HENRI MOISSAN and JAMES DEWAR (*Compt. rend.*, 1903, 136, 785—788. Compare this vol., ii, 360).—In carrying out experiments at such low temperatures as -190° , two difficulties are met with; moisture is condensed from the atmosphere and forms a layer of ice around the cooled substances which protects them from attack, and, secondly, layers of insoluble products of the reaction are formed and preserve the substances from further action.

In investigating the action of liquid fluorine at -187° on various substances, the carefully dried substance contained in a narrow, sealed glass tube was cooled to -190° and then the tube broken inside a crystal tube containing the liquid fluorine.

Although iodine takes fire in fluorine at the ordinary temperature, no reaction occurs at this low temperature. A mixture of liquid oxygen and fluorine can be separated by distillation. Sulphur burns in liquid fluorine with an intensely blue flame, the whole apparatus being broken by the elevation of temperature; sulphur hexafluoride is formed. Selenium and fluorine combine explosively at this low temperature, whilst tellurium is not attacked. Nitrogen and fluorine have no action on one another at any temperature. Red phosphorus and fluorine combine with development of heat, phosphorus pentafluoride being produced. Arsenic and fluorine react violently, the arsenic burning with a blue flame. Antimony is not attacked. The different varieties of carbon, crystalline silicon, and amorphous boron do not react with fluorine, but wood charcoal and soot become incandescent in liquid fluorine. Sodium does not lose its lustre, but it becomes surrounded by a transparent layer of sodium fluoride; potassium at first has no action, but after a few seconds a violent explosion occurs.

Potassium iodide does not react with liquid fluorine below its

boiling point, but at this temperature a rapid action sets in with development of heat, the iodine being displaced by fluorine. Under the same conditions, mercuric iodide and potassium ferrocyanide are not attacked. Arsenious oxide is not changed by fluorine; the same holds for silica and boric anhydride, but lime reacts violently, becoming incandescent, the apparatus finally being destroyed. Calcium carbide is without action.

Anthracene and liquid fluorine react with explosive violence at -187° , carbon being deposited; under the same conditions, iodoform, sugar, mannitol, and morphine are not decomposed by fluorine. K. J. P. O.

Preparation of Thionyl Chloride. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 139455).—Thionyl chloride may be prepared by adding sulphur trioxide to ordinary sulphur chloride at a temperature of $75-80^{\circ}$, according to the equation $\text{SO}_3 + \text{S}_2\text{Cl}_2 = \text{SOCl}_2 + \text{SO}_2 + \text{S}$. Chlorine is passed in continuously in order to reconvert the sulphur produced into sulphur chloride. In this way, an almost theoretical yield is obtained, and the practical inconveniences attending the use of higher chlorides of sulphur are avoided. C. H. D.

Compounds of Selenates with Iodates, Phosphates, and Arsenates. RUDOLPH F. WEINLAND and GEORG BARTTLINGCK (*Ber.*, 1903, 36, 1397—1404).—*Selenate Iodates*.—These are of two types, $2\text{SeO}_3, \text{I}_2\text{O}_5, 2\text{M}_2\text{O}, \text{H}_2\text{O}$ (or $\text{MHSeO}_4, \text{MIO}_3$) and $2\text{SeO}_3, 3\text{I}_2\text{O}_5, 2\text{M}_2\text{O}, 5\text{H}_2\text{O}$ (or $\text{MHSeO}_4, 2\text{HIO}_3, \text{MIO}_3, \text{H}_2\text{O}$); they do not separate from solutions containing the theoretical quantities of the constituents, but the selenic acid has to be in excess so as to prevent the acid iodate from being formed. The second type is obtained from solutions containing a minimum of alkali. *Potassium selenate iodate*, $2\text{SeO}_3, \text{I}_2\text{O}_5, 2\text{K}_2\text{O}, \text{H}_2\text{O}$, forms flat, transparent, four-sided prisms, and the *ammonium* salt is similar. *Potassium selenate tri-iodate*, $2\text{SeO}_3, 3\text{I}_2\text{O}_5, 2\text{K}_2\text{O}, 5\text{H}_2\text{O}$, forms small, colourless, thick, well-developed prisms, and closely resembles the analogous *rubidium* and *ammonium* salts.

Selenate Phosphates and Selenate Arsenates.—These compounds exist in two types, $2\text{SeO}_3, \text{P}_2\text{O}_5(\text{As}_2\text{O}_5), 2\text{M}_2\text{O}, 3\text{H}_2\text{O}$ or $\text{MH}_2\text{P}(\text{As})\text{O}_4, \text{MHSeO}_4$, and $5\text{SeO}_3, \text{P}_2\text{O}_5(\text{As}_2\text{O}_5), 3\cdot5\text{K}_2\text{O}, 5\cdot5\text{H}_2\text{O}$ or $2\text{MH}_2\text{P}(\text{As})\text{O}_4, 5\text{KHSeO}_4, \text{H}_2\text{O}$; the former is analogous to the sulphate phosphates (Jacquelin, *Ann. Chim. Phys.*, 1839, [ii], 70, 317) and the sulphate arsenates (Friedheim, *Abstr.*, 1894, ii, 314), but the latter has no true analogue. In the case of potassium, selenate phosphates and selenate arsenates of both types were prepared, but of rubidium and ammonium only salts of the first formula could be obtained; the *selenate monophosphates* form hard, colourless leaflets, and the *selenate diphosphates* transparent, rod-shaped crystals. W. A. D.

Oxidation of Atmospheric Nitrogen by Electric Discharges. FRANZ VON LEPEL (*Ber.*, 1903, 36, 1251—1258. Compare Muthmann and Hofer, this vol., ii, 206).—An increased yield of nitric acid is obtained by rotating a pair of anodes about a single cathode, but the yield decreases again if too many anodes are used or if the speed of

rotation is too great; the best speed must be determined experimentally for each form of apparatus. The best results are obtained when the anode is a point and the cathode a plate. The materials used for the electrodes are also important; copper (+) and carbon (-) is apparently the best combination, but with a zinc anode a gold cathode gives the best yield, with an iron anode a cathode of manganese dioxide is best, and with a platinum anode a cathode of manganese dioxide or carbon. The liquid used for absorbing the nitrogen oxides has an important influence on the yield, the best results being given by potassium carbonate and the worst by pure water. By collecting the products separately, it was found that nitric acid is produced almost exclusively in the absorption chamber and not in the chamber in which the combustion is carried on. Oxygen mixed with the air increases the yield of acid, hydrogen has a slightly favourable effect, and the use of ozonised air gives only slight increases in the yield. The nature of the flame is, however, the most important factor in determining the yield; the first product is nitrogen monoxide, an endothermic compound, and it is important that this should be removed as rapidly as possible from the flame.

T. M. L.

Action of Liquefied Ammonia on Phosphorus. ALFRED STOCK (*Ber.*, 1903, 36, 1120—1123).—When yellow phosphorus is heated above its melting point with excess of liquefied ammonia, it is converted into a fine, black powder, which contains phosphorus, nitrogen, and hydrogen. It turns intensely orange-red in moist air, the change occurring very quickly in presence of acids; the black colour is regenerated by addition of ammonia. The black substance is possibly P_2NH_2 and the red P_4O .

Schenck's experiments (this vol., ii, 363) are criticised.

A. McK.

Pyrophosphorous Acid. VICTOR AUGER (*Compt. rend.*, 1903, 136, 814—815).—Amat's attempts (*Abstr.*, 1890, 438) to prepare pyrophosphorous acid from pyrophosphites leads only to the formation of phosphorous acid. Kraut (*Annalen*, 1871, 158, 332) and Gautier (*Compt. rend.*, 1873, 76, 49) did not obtain this acid by the action of phosphorous trichloride on phosphorous acid; Besson (*Abstr.*, 1898, ii, 160) showed that phosphorous trichloride reacted with a small quantity of water to form phosphorous and hydrochloric acids. *Pyrophosphorous acid*, $H_4P_2O_5$, is easily prepared by vigorously shaking together phosphorous acid and phosphorous trichloride, the latter being in large excess, and the temperature being maintained at 30—40°; the clear liquid, thus obtained, is also produced by passing carbon dioxide saturated with the vapour of phosphorous trichloride into a paste made by moistening the trichloride with water. The liquid is placed over phosphoric oxide and potassium hydroxide in a desiccator, when it solidifies to crystals, which are very deliquescent and melt at 38°. When moistened with water, this acid is immediately converted into phosphorous acid; on heating to 100°, it becomes yellowish-red, and at 130° hydrogen phosphide is evolved.

K. J. P. O.

Action of Hydrogen on the Arsenic Sulphides in the presence of Antimony, and on Antimony Trisulphide in the presence of Arsenic. HENRI PÉLABON (*Compt. rend.*, 1903, 136, 812—813. Compare Abstr., 1902, ii, 253).—When realgar, 0.5 gram, is heated at 620° with quantities of antimony varying from 0.1 to 3.0 grams in an atmosphere of hydrogen, hydrogen sulphide is formed, and has a partial pressure which amounts to 0.834 of the total pressure for the lowest proportion of antimony used, and 0.615 of the total pressure for the largest amount of antimony; the partial pressure of the hydrogen sulphide decreases with increase of the proportion of antimony, but the rate of decrease becomes much slower, after the amount of antimony present is in excess of that equivalent to the sulphur in the realgar. When 0.4 gram of antimony is used, the solid left in the tube after the experiment consists of two parts, one of which is antimony sulphide containing a trace of antimony, and the other an alloy of antimony and arsenic. Arsenic sulphide is not present.

When, instead of realgar, a mixture (0.5 gram) of arsenic and sulphur in the proportion of $\text{As}:\text{S}_2$ is used, and quantities of antimony varying from 0.2 to 3.0 grams, the temperature being the same as in the previous case, the partial pressure of the hydrogen sulphide is initially 0.94, and decreases rapidly until the amount of antimony present is equivalent to the sulphur; after that point is reached, the rate of decrease of the partial pressure diminishes.

In experiments made with antimony trisulphide and arsenic at 630° , 0.5 gram of the sulphide being used and the amount of arsenic increasing from 0 to 3.0 grams, the proportion of the hydrogen sulphide in the gas phase increases from 0.711 to 0.761.

K. J. P. O.

Arsenious Acid. JAN VON ZAWIDZKI (*Ber.*, 1903, 36, 1427—1436).—Molecular weight determinations show that when arsenious oxide is dissolved in water the resulting molecules contain only a single atom of arsenic. The acid is a poor conductor, and appears to be very slightly dissociated; the molecular conductivity of the sodium salt, NaH_2AsO_3 , determined in presence of *N*/32 arsenious acid in order to diminish hydrolytic dissociation, resembles that of the sodium salt of a monobasic acid; the increase of mol. conductivity at extreme dilutions might be explained as due to further dissociation of the H_2AsO_3 ion, but is regarded by the author as caused by hydrolysis and oxidation. This view is in agreement with the observations of Thomsen that 137.8 Cal. are liberated in neutralising As_2O_3 with 2NaOH , and only 12.9 Cal. on adding a further 2NaOH , and establishes the view that arsenious acid is essentially a feeble monobasic acid. It is also an extraordinarily feeble base, but the basic properties are too slight to allow of definite measurements.

T. M. L.

Preparation of Solid Carbon Dioxide. NICOLAE TECLU (*J. pr. Chem.*, 1903, [ii], 67, 423—425).—To exhibit the formation of solid carbon dioxide, a stream of liquid carbon dioxide issuing from a jet is directed into a glass tube connected with a series of bulbs. The formation of the solid can be seen taking place in the bulbs. A form

of apparatus suitable for the preparation of large quantities of solid carbon dioxide is described. G. Y.

Equilibrium between Iron Oxides and Carbon Monoxide and Carbon Dioxide. EMIL BAUR and A. GLAESSNER (*Zeit. physikal. Chem.*, 1903, 43, 354—368).—The equilibria which may be established by conducting carbon monoxide or carbon dioxide over iron are represented by the equations: $\text{Fe} + \text{CO} = \text{FeO} + \text{C}$; $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$; $\text{C} + \text{CO}_2 = 2\text{CO}$. The reaction $\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$ is also one of equilibrium. The equilibrium relationships were determined by heating the solid in an atmosphere of carbon monoxide or carbon dioxide in a boat contained in a porcelain tube connected with a gas-burette. The tube was electrically heated, and the temperature was measured by a thermoelement. After the equilibrium had been established, the gas was drawn off and analysed. The solids examined were: ferrosferriic oxide and ferrous oxide, and ferrous oxide and iron. The equilibrium curve in the first case exhibits a maximum at 490° , when the gas phase contains 47 per cent. of carbon monoxide. This indicates the temperature at which ferrosferriic oxide is most difficultly reduced. In the second case, the curve shows a minimum point at 680° , when 59 per cent. of carbon monoxide is present; this corresponds with the temperature at which ferrous oxide is most easily reduced to iron.

The results are plotted graphically along with Boudouard's values for the equilibrium between carbon and carbon dioxide, and from the points where the curves cut it is deduced that at atmospheric pressure, carbon monoxide, carbon dioxide, ferrous oxide, ferrosferriic oxide, and carbon can exist side by side at 647° , and the three solids are in equilibrium at 685° . Above 685° , carbon and iron can exist together, and below 647° carbon and ferrosferriic oxide.

These conclusions, derived from the curves, have been experimentally verified.

When applied to the reactions which take place in the blast furnace, the results show that the reductions of ferrosferriic oxide and ferrous oxide must take place at different zones which are characterised by different contents of carbon monoxide. Iron in contact with a gas rich in carbon monoxide at temperatures below 647° is oxidised and carbon is deposited, but no carbon can be deposited from the gas at a temperature higher than 680° .

The heat of formation of ferrosferriic oxide at 490° under constant pressure is calculated to be 267,380 Cal., and that of ferrous oxide at 680° is 67,350 Cal. J. McC.

The Decomposition of Carbon Monoxide and Chemical Equilibrium in the Blast Furnace. RUDOLF SCHENCK and F. ZIMMERMANN (*Ber.*, 1903, 36, 1231—1251. Compare Boudouard, *Abstr.*, 1899, ii, 287, 365, 417, 595, 596; 1900, ii, 199; 1901, ii, 151, 314, 383, 646).—The reversible reaction $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$ has been studied as a time reaction in the presence of metals and metallic oxides. The apparatus consisted of an air thermometer in which the

metal or metallic oxide could be introduced and then sealed. This vessel was attached to a series of two manometers and three taps, one of which was a three-way cock. By this means, the apparatus could be readily exhausted, filled, and emptied.

The metals employed, namely, iron, cobalt, and nickel and their oxides, were deposited in a fine state of division on pumice, which had been reduced in a current of pure hydrogen (from aluminium and hydrochloric acid) and then extracted with dilute hydrochloric acid. By this process, the whole of the original iron compounds contained in the pumice were removed. The oxides were obtained by saturating the pumice with solutions of the metallic nitrates and then strongly heating. To obtain the deposit of metal, the pumice, with the oxide, was reduced in a stream of pure hydrogen. The oxides of cobalt and nickel completely oxidise carbon monoxide to the dioxide at 445° and are themselves reduced to the metallic state, so that no alteration in pressure occurs. With ferric oxide, only part of the carbon monoxide is oxidised, and a slight reduction in pressure occurs owing to the catalytic decomposing action of the metallic iron produced on the monoxide. It has been found that with a gaseous mixture containing one volume of the monoxide to four of the dioxide no reduction of the ferric oxide occurs and the pressure remains constant.

The carbon dioxide obtained by Boudouard must have been due to the oxidation of the carbon monoxide by the ferric oxide and not to the catalytic decomposition of the monoxide. Finely divided metals accelerate the decomposition of the monoxide into carbon and dioxide in a remarkable manner.

With nickel at a temperature of 445° , the reaction has been shown to be bimolecular and should be represented as $2\text{CO} = \text{C} + \text{CO}_2$; at 310° and 360° , however, the reaction appears to be unimolecular and probably occurs in two stages, namely, $\text{CO} = \text{C} + \text{O}$ and then $\text{CO} + \text{O} = \text{CO}_2$, the second reaction proceeding much more rapidly than the first. When a number of experiments are performed in the same vessel without removing the carbon produced, the value for the velocity constant is always higher.

The reaction does not appear to be complete, but is reversible, and a state of equilibrium is established even at temperatures of 445° (compare Boudouard, *loc. cit.*).

When cobalt is employed, the numbers agreed with neither a uni- nor a bi-molecular reaction. This is probably due to iron contained as an impurity in the cobalt.

When iron is employed, the pressure never becomes absolutely constant so long as any gas is present, and ultimately the whole of the carbon present is deposited in the free state and ferric oxide is formed. It would appear that the iron first reacts as a catalyser, decomposing the carbon monoxide into carbon and dioxide. When the concentration of the dioxide has increased, and that of the monoxide decreased, to a certain limit, the metal begins to reduce the dioxide, and the two reactions then proceed simultaneously, so that the composition of the gas remains the same. Experiments made at 360° and 445° indicate that the reaction is unimolecular, but that at 508° it becomes bimolecular.

The compositions of the gaseous mixtures are as follows :

360°	10.5 per cent. monoxide and 89.5 dioxide	
445	52.8 „ „	47.2 „
508	47 „ „	52.9 „

The numbers obtained at 360° probably indicate the presence of some oxide other than ferric oxide. J. J. S.

Preparation of Potassium from Fused Potassium Hydroxide.

RICHARD LORENZ and W. CLARK (*Zeit. Elektrochem.*, 1903, 9, 269—271).—The authors regard the difficulty of the preparation of potassium by electrolysis of fused potassium hydroxide as resulting from the great tendency of the metal to dissolve or form a metallic “fog” in the electrolyte (compare Abstr., 1901, ii, 142, and 538). When the solution of metal is prevented from diffusing away from the cathode by means of a porous partition (a magnesite crucible is used), good yields of potassium are obtained. For example, 15.5 grams of potassium were obtained with 13.4 amperes and 15 volts in 71 minutes, or 58 per cent. of the theoretical current efficiency.

This method does not yield barium from the fused hydroxide ; nothing but barium oxide is produced, $\text{Ba}(\text{OH})_2 + \text{Ba} = 2\text{BaO} + \text{H}_2$. Sodium and lithium were prepared from the chlorides, however, although the magnesite crucible is rapidly attacked. An experiment with barium chloride was unsuccessful. T. E.

The Dependence of the Reactive Power of Potassium and Sodium Hydroxides on the Concentration. WILHELM VAUBEL (*Zeit. angew. Chem.*, 1903, 16, 389—391).—Potassium manganate is not stable in solution unless alkali is present. The minimum quantity of sodium hydroxide required to render the solution stable is 0.1 per cent., and of potassium hydroxide 0.04 per cent. A solution of calcium hydroxide also hinders the decomposition, but sodium carbonate, sodium chloride, and disodium hydrogen phosphate do not appear to prevent the transformation into permanganate. Potassium permanganate behaves inversely. It is quite stable in solutions containing up to 27.80 per cent. of sodium hydroxide, but if more of the alkali be present potassium manganate is formed. The author claims that this varying action of alkali according to concentration can only be due to the formation of hydrates or of complex molecules formed by the hydroxide itself.

Not only does the rate of absorption of oxygen by organic hydroxy-derivatives depend on the concentration of the alkali present, but the quantity absorbed is also influenced by this concentration. With quinol, the greatest absorption takes place when the solution contains 4.5 per cent. of sodium hydroxide. With catechol, the influence of the sodium hydroxide concentration is only small. In the case of pyrogallol, the maximum absorption is obtained when the solution contains 0.5 to 2.25 per cent. of sodium hydroxide, and with gallic acid the maximum is found when 4.5 per cent. of the alkali is present.

After the absorption of oxygen by pyrogallol and alkali, a compound of the formula $\text{C}_{26}\text{H}_{17}\text{O}_7(\text{OH})_3$ was isolated. J. McC.

Preparation of Alkali Nitrites. CHEMISCHE FABRIK GRÜNAU, LANDSHOFF & MEYER (D.R.-P. 138029).—Sodium nitrate, mixed with 5 per cent. of sodium hydroxide, is fused, and 5—10 per cent. more than the theoretical quantity of sodium sulphite gradually added, the temperature being maintained at 320° to 420° . The product is extracted with mother liquor from a previous crystallisation of nitrite, and by a suitable arrangement of extracting vessels in series the nitrite may be obtained free from sodium sulphate. C. H. D.

Electrolytic Reduction of Potassium Chlorate. DONATO TOMMASI (*Compt. rend.*, 1903, 136, 1005—1006. Compare Bancroft, *Trans. Amer. Electrochem. Soc.*, 1, 65; Burrows, this vol., ii, 7; and Brochet, this vol., ii, 210).—When a solution of potassium chlorate containing sulphuric acid is electrolysed between platinum electrodes, perchlorate is formed at the anode, but no chloride is produced at the cathode. If a zinc, copper, or lead anode is used, potassium chloride is formed there, but if the cathode be of platinum no reduction takes place round this electrode. The reduction at the anode must be attributed to the metal and not to the hydrogen ($\text{KClO}_3 + 3\text{Zn} = \text{KCl} + 3\text{ZnO}$). Under the same conditions, perchlorate is not reduced, even when a zinc anode is used.

If some zinc is added to a solution of cupric sulphate containing a dissolved chlorate, decomposition takes place and a chloride is formed; at the same time, some of the cupric salt is reduced to the cuprous condition.

Potassium chlorate is reduced by the action of zinc on mercuric nitrate, or of tin on cupric sulphate, but under no conditions is it reduced by sodium amalgam. In presence of acetic acid, zinc does not reduce the chlorate, but the zinc-copper couple causes partial reduction. J. McC.

Hydrates of Barium Hydroxide. O. BAUER (*Zeit. angew. Chem.*, 1903, 16, 341—350).—Besides anhydrous barium hydroxide, compounds containing 16, 8, and $1\text{H}_2\text{O}$ respectively are known. The preparation of a new hydrate containing $3\text{H}_2\text{O}$ is described. Ordinary crystallised barium hydroxide, containing $8\text{H}_2\text{O}$, melts in its water of crystallisation at 78° under a pressure of 732 mm. When the temperature is gradually raised, boiling begins at 103° , and at 108.5° crystals of the trihydrate, $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ separate. The new hydrate crystallises in the rhombic system, differing in this respect from the tetragonal octahydrate; it forms transparent crystals of diamond lustre, which quickly disappears on exposure to air. In dry air, it passes into the monohydrate. A. McK.

Action of Metallic Magnesium on Aqueous Solutions. LOUIS KAULENBERG (*J. Amer. Chem. Soc.*, 1903, 25, 380—392).—The action of magnesium on aqueous solutions of metallic salts has been studied by Tommasi (Abstr., 1900, ii, 16), whilst Lemoine (Abstr., 1899, ii, 656) has examined its action on aqueous solutions of magnesium salts. In those cases, hydrogen is evolved with varying

rapidity. Lemoine supposes that solutions of magnesium salts are slightly decomposed into magnesium hydroxide and free acid, which acts on the metal to form hydrogen and a basic salt; the latter breaks up into normal salt and magnesium hydroxide, which separates out. The author points out that Lemoine's conception is inadequate, since magnesium salts are neutral to indicators at the outset, and that, soon after the magnesium is introduced, the solution turns alkaline and the liberation of hydrogen proceeds. In the case, however, of salts of the heavy metals, where a small quantity of free acid is actually liberated, Lemoine's conception may hold.

The rate with which hydrogen is evolved from various aqueous solutions by the action of magnesium has been examined by the author; the rapidity varied with each solution tested and was different from that observed with pure water. Solutions of alcohol, glycerol, sucrose, mannitol, carbamide, various sodium, magnesium, and potassium salts, sulphuric acid, and hydrochloric acid were employed. Normal solutions of sodium and potassium hydroxide yielded no hydrogen in 24 hours. Hydrogen was liberated from the glycerol solution more slowly, and from the alcohol solution much more vigorously, than from pure water. Sodium chloride solution was much more vigorous than sodium sulphate of equivalent strength. The single differences of potential between magnesium and various salt solutions were measured.

An alkaline reaction is imparted to solutions of various salts by the magnesium soon after it has been immersed in them, and yet this alkalinity does not interfere with the evolution of hydrogen. There is again no reason to suppose that magnesium chloride suffers more hydrolytic decomposition than the chlorides of calcium, strontium, and barium, yet solutions of the latter salts are acted on only feebly by magnesium, whilst from magnesium chloride hydrogen is rapidly evolved. The inadequacy of the electrolytic dissociation theory with reference to these and other observations is considered. The facts are, however, very readily explained on the basis that solutions are chemical combinations of solvent and solute in variable proportions.

A. McK.

Preparation of Crystallised Zinc Sulphide and Cadmium Sulphide. GEORGES VIARD (*Compt. rend.*, 1903, 136, 892—893).—When a current of carbon dioxide carrying the vapour of zinc chloride is passed over stannous sulphide heated to redness, zinc sulphide is formed and is deposited in colourless, prismatic crystals. Needle-shaped or tabular crystals of cadmium sulphide can be formed in the same way, using the vapour of cadmium chloride; the crystals vary in colour between brownish-red and yellowish-orange.

Antimony sulphide may be used in place of stannous sulphide, but the crystals are, as a rule, not so good.

J. McC.

Cathodic Deposition of Lead. KARL ELBS and F. W. RIXON (*Zeit. Elektrochem.*, 1903, 9, 267—268).—Lead is sometimes deposited in large, shining plates, sometimes in the form of a sponge consisting of microscopic needles. The authors show that the difference is due to

the presence or absence of plumbic salt in the electrolyte, the spongy deposit being always obtained when plumbic salt is present. Small quantities of plumbic salts may be estimated colorimetrically by means of a solution of starch and potassium iodide. The acid in a lead accumulator always contains plumbic sulphate, formed by the reaction $\text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{Pb}(\text{SO}_4)_2 + 2\text{H}_2\text{O}$. The reduction of this plumbic sulphate by the spongy lead plate explains the slow discharge of a well-insulated accumulator cell.

T. E.

Thiocarbonates of Heavy Metals. KARL A. HOFMANN and F. HÜCHTLEN (*Ber.*, 1903, 36, 1146—1149).—The salt previously described as cupric trithiocarbonate ammonia (Abstr., 1897, ii, 321) is really *cuprous ammonium thiocarbonate*, CS_3CuNH_4 ; the analogous *cuprous potassium thiocarbonate*, CS_3CuK , prepared by adding a concentrated solution of cupric chloride to carbon disulphide dissolved in aqueous potassium hydroxide at 0° , crystallises in thick plates having a greenish lustre. Both salts are converted by acetic acid or, better, by sodium hydrogen sulphite, into the salt $\text{C}_2\text{S}_7\text{Cu}_4$, which forms six-sided plates with a bronze-like lustre and is insoluble in water.

The compound, $\text{CS}_3\text{Cu}_2 \cdot 2\text{KCN} \cdot 2\text{H}_2\text{O}$, prepared by dissolving the salt CS_3CuNH_4 in aqueous potassium cyanide at 0° , crystallises in lustrous, blood-red plates or stellate aggregates of prisms.

The compound $\text{CS}_2\text{O} \cdot \text{CoO} \cdot \text{SO}_2\text{H} \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, obtained by dissolving cobalt thiocarbonate in aqueous sodium hydrogen sulphite at 0° , crystallises from water as a dark green powder; the analogous *potassium* compound, $\text{CS}_2\text{O} \cdot \text{CoO} \cdot \text{SO}_2\text{H} \cdot 2\text{K}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, resembles it.

W. A. D.

Change of Colour shown by Mercuric Iodides at Different Temperatures. DÉSIRÉ GERNEZ (*Compt. rend.*, 1903, 136, 889—891).—The transition point of red and yellow mercuric iodides lies about 126° , but the varieties may be maintained indefinitely at temperatures outside their respective ranges of stability provided that the other form is entirely absent.

When the red modification is heated, it slowly becomes yellow at 126° , and at 200° it is reddish-orange in colour. When the red variety is cooled, it assumes more of a yellow tinge, and likewise becomes reddish-orange at the temperature of boiling liquid air. The colour changes observed when the two varieties are cooled in liquid air show that they behave as two entirely different substances, and, contrary to an opinion which has been expressed, the red, quadratic modification does not pass into the yellow, rhombic form.

J. McC.

Red and Yellow Mercuric Oxides and the Mercuric Oxychlorides. EUGENE P. SCHUCH (*Amer. Chem. J.*, 1903, 29, 319—340).—Yellow mercuric oxide crystallises in microscopic, square tablets. If the crystals are left in contact with the liquid in which they are precipitated or with solution of sodium or potassium chloride, they increase in size and the colour changes from pale yellow to an orange,

and, after some weeks, to a red tint. When the crystals of the yellow oxide are boiled with aqueous solutions of salts, they are converted into the prismatic form of the red oxide; the same change takes place when the dry yellow oxide is heated at $250\text{--}600^\circ$ for 8—24 hours. The colour of the oxide does not afford trustworthy evidence as to which form is present, since the tabular crystals of the yellow oxide sometimes exhibit a deeper colour than the prismatic crystals of the red variety. The yellow oxide is not a hydroxide, as stated by Carnelley and Walker (*Trans.*, 1888, 53, 80), but only contains about 0.5 per cent. of water; both oxides have the same composition. The densities of two specimens of the yellow oxide were found to be 11.08 and 11.11 at 27.5° ; of two specimens of the red oxide, one had a density 11.03 at 27.5° , and the other a density 11.08 at 28.5° . Since, at higher temperatures, the yellow oxide changes to the red, the dissociation pressure of the yellow variety should be greater than that of the red, and this has been found to be the case. At $300\text{--}320^\circ$, the dissociation pressure of the yellow oxide is 760 mm. or more, whilst that of the red oxide does not exceed 400 mm. at that temperature.

The mercuric oxychlorides have been studied by Millon (*Ann. Chim. Phys.*, 1846, [iii], 18, 372), who obtained them by the action of alkali hydrogen carbonate on solutions of mercuric chloride, and by Roucher (*ibid.*, 1849, [iii], 27, 353), who prepared them by the action of yellow or red mercuric oxide on solutions of mercuric chloride. The work of these investigators was repeated by Thümmel (*Abstr.*, 1889, 1051). Mercuric oxychlorides have also been obtained by André by fusing mercuric oxide with mercuric chloride. The whole of this work has been reinvestigated; the results of Thümmel are generally confirmed, whilst those of André are found to be untrustworthy, the compounds which he prepared probably having been impure.

The compound $2\text{HgCl}_2, \text{HgO}$ (trimercurioxychloride) forms large, isometric, rhombic dodecahedra, and has a sp. gr. 6.42. The red modification of the compound $\text{HgCl}_2, 2\text{HgO}$ (trimercuridioxychloride) forms short, hexagonal prisms with pyramidal ends and has a sp. gr. 8.16; it cannot be converted into the black, amorphous form by heating, as stated by Thümmel. The black modification has a sp. gr. 8.53. The compound $\text{HgCl}_2, 3\text{HgO}$ (tetramercuritrioxychloride) crystallises in prisms and has a sp. gr. 7.93; when it is heated with water, the compound $\text{HgCl}_2, 4\text{HgO}$ (pentamercuritetroxychloride) is produced, which forms yellow, hexagonal plates and has a sp. gr. 9.008. The brown, amorphous modification of the latter compound has a sp. gr. 9.050. In repeating André's experiments, only two distinct oxychlorides could be obtained; these were modifications of the compounds $\text{HgCl}_2, 2\text{HgO}$ and $\text{HgCl}_2, 4\text{HgO}$, and had the sp. gr. 8.43 and 9.107 respectively.

E. G.

Ceric Chromate. PHILIP E. BROWNING and CHARLES P. FLORA (*Amer. J. Sci.*, 1903, [iv], 177—178).—The authors prepared ceric chromate from the cerium earths according to Böhm's method (this vol., ii, 149), but used a decided excess of chromic acid. The product obtained, $\text{Ce}(\text{CrO}_4)_2, 2\text{H}_2\text{O}$, was a bright scarlet, crystalline salt which,

under the microscope, appears homogeneous. Its form is orthorhombic, the prevailing habit being prismatic. The crystals are decomposed by water, lose chromic acid, and become orange-yellow. They may be heated at 150° without loss of weight; between 150° and 180° , they lose water and become brownish-red without seriously altering their exterior form, but above 180° they are decomposed. L. DE K.

Cementation of Iron. GEORGES CHARPY (*Compt. rend.*, 1903, 136, 1000—1002).—The cementation agents examined were: graphite, wood charcoal (both pure and mixed with alkaline-earth carbonates), animal charcoal, coal gas, carbon monoxide, cyanogen, and potassium cyanide. Steel cut into small pieces was heated in an electric furnace in contact with one of these agents, and the temperature was determined by a thermo-element. The time taken for the metal to become saturated with carbon is a function of the size of the pieces of metal, of the nature of the cementation agent, and of the temperature. When saturation has been reached, crystals of cementite (iron carbide) separate out at certain points on account of the fluctuations of temperature which it is impossible to avoid. The iron takes up carbon to such an extent that the product contains 6.7 per cent. of carbon. At a high temperature (1000°), the iron carbide is decomposed and graphite separates; the free iron may then take up more carbon, which is in turn deposited as graphite, and thus a quantity of iron may transform an unlimited amount of carbon. The cementation, therefore, is not limited by the solubility of carbon in iron. J. McC.

Corrosion of Iron. WILLIS R. WHITNEY (*J. Amer. Chem. Soc.*, 1903, 25, 394—406).—Iron oxidises or dissolves in all solutions containing appreciable quantities of hydrogen ions, and this electrochemical relationship between iron and hydrogen is the primal cause of rusting. Iron dissolves in pure water. It is generally supposed that the presence of carbon dioxide is necessary for the corrosion of iron, but an experiment is described where it is shown that this view is incorrect. The corroding action of carbon dioxide on iron is a cyclic one, where even a trace of carbon dioxide may cause the dissolution of an unlimited quantity of iron without losing its corrosive power.

A. McK.

Oxidation by Chromic Acid in Presence of other Acids. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1903, [iii], 29, 306—314).—By comparing the periods of time necessary for the decolorisation of calico dyed with indigo by solutions containing various quantities of chromic and oxalic acids, it was observed that the velocity of oxidation, when the amount of chromic acid is constant, is proportional to the amount of oxalic acid present, whilst when the concentrations of both acids vary, although their relative proportions are constant, the velocity of oxidation is proportional to the square of the concentration of the oxalic acid, and generally the velocity varies with the product of the concentrations of the reacting acids. These relationships hold so long as the solutions contain not more than 1 mol. of oxalic acid for each mol. of chromic acid. Molecular solutions of the two acids give no

blue coloration with hydrogen peroxide and ether, and it is suggested that they contain a compound of the formula $\text{C}_2\text{O}_4 \cdot \text{CrO}_2$, which is unstable and liberates ozone in the presence of reducing agents.

A similar acceleration of the rate of oxidation of indigo by chromic acid is brought about by sulphuric acid, and in this case the compound $\text{SO}_4 \cdot \text{CrO}_2$, which is more stable than the corresponding oxalic acid derivative, is regarded as existing in solutions of the two acids. Experiments with arsenious oxide showed that chromic acid has the same oxidising power in presence of small and very large quantities of sulphuric acid.

Accelerations of the rate of oxidation by chromic acid are also brought about by tartaric, citric, nitric, chloric, iodic, ferrocyanic, and ferricyanic acids.

When chromic and oxalic acids in the proportions of 1 mol. of the former to more than 3 mols. of the latter are dissolved together, the velocity of reduction of the chromic by the oxalic acid is directly proportional to the excess of the latter, and inversely proportional to the dilution.

T. A. H.

[Non-]Existence of Perchromic Acid. HARRISON E. PATTEN (*Amer. Chem. J.*, 1903, 29, 385—386).—When a saturated solution of potassium dichromate is cooled to -16° and treated with 2 per cent. solution of hydrogen peroxide at the same temperature, a white, solid substance separates and the solution turns blue. If a cold saturated solution of sodium acetate is added to this solution, it assumes the lake colour of chromous acetate, and if left for half an hour the green colour of chromic acetate appears. Solid chromous acetate may be obtained by extracting the blue solution with ether and adding sodium acetate to the blue ethereal solution. The electrical conductivity of the blue ethereal solution of "chromous oxide" was found to be less than 2×10^{-8} at 0° . The simplest explanation of these facts is that chromic acid is reduced to the chromous state by hydrogen peroxide, and a higher oxide of hydrogen is produced. The existence of an oxide of hydrogen higher than the dioxide is thus confirmed, whilst the existence of perchromic acid is rendered extremely doubtful.

E. G.

A New Class of Peruranates. JULES ALOY (*Bull. Soc. chim.*, 1903, [iii], 29, 292—294. Compare *Abstr.*, 1902, ii, 609).—When hydrogen peroxide is added to a solution of uranium salt, peruranic hydroxide is precipitated (Fairley, this Journal, 1877, 31, 127); this, when suspended in a solution of hydrogen peroxide containing a little alcohol, is converted by the addition of an alkali hydroxide into the corresponding alkali peruranate. These peruranates are heavy, red, crystalline solids, which evolve oxygen slowly at the ordinary temperature and rapidly at 100° . They are decomposed by water with the formation of insoluble uranates, and by hydrochloric acid with the production of chlorine, whilst nitric acid liberates peruranic anhydride. The potassium and sodium salts are represented by the formulæ $\text{K}_2\text{UO}_5 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{UO}_5 \cdot 5\text{H}_2\text{O}$ respectively.

T. A. H.

Preparation of Metallic Thorium. SIEMENS & HALSKE (D.R.-P. 133959).—Metallic thorium may be prepared by the action of potassium or sodium vapour on the vapour of volatile organic compounds of thorium, such as the thorium derivative of acetylacetonate. The process is carried out in an indifferent or reducing atmosphere, metallic thorium being deposited in a pure state, and potassium- or sodium-acetylacetone being formed. By passing the mixed vapours, at a temperature somewhat below that required for combination, over a metal or carbon filament, strongly heated by an electric current, the filament receives a coherent coating of thorium, and may be employed in the manufacture of incandescent lamps. C. H. D.

Pervanadic Acid. L. PISSARJEWSKY (*Zeit. physikal. Chem.*, 1903, 43, 173—178).—Pervanadic acid is formed when vanadium pentoxide is added to hydrogen peroxide in aqueous dilute sulphuric acid solution; a red solution is thus obtained which deposits yellow crystals, the solution of which is acid, and decomposes slowly with evolution of oxygen. It is found that one mol. of hydrogen peroxide is used per atom of vanadium, and the author gives the formula HVO_4 or $\text{VO}_2(\text{O}_2\text{H})$ to the pervanadic acid. After a time, it slowly decomposes with formation of either HVO_3 , $\text{H}_2\text{V}_4\text{O}_{11}$, or $\text{H}_2\text{V}_6\text{O}_{16}$, all of which also, by treatment with hydrogen peroxide, form pervanadic acid (compare Abstr., 1902, ii, 326, 565, 663; this vol., ii, 66). L. M. J.

Atomic Weight of Antimony. ERNST COHEN and TH. STRENGERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 543—550).—Popper's experiments (Abstr., 1886, 856) have been repeated. The amount of antimony separated by electrolysis of hydrochloric acid solutions of antimony trichloride was determined. Antimony rods were used as anodes and thin platinum wires as cathodes. The antimony deposited on the platinum was freed from antimony chloride by heating in a special tube. The results cannot be used for calculating the atomic weight of antimony because the equivalent found increases with the concentration of the solution electrolysed. J. McC.

Use of Polyhydroxyphenols, Phenolic Acids, Aldehydes, and Phenolic Aldehydes in the Preparation of Colloidal Solutions of Gold, Platinum, and Silver. LUDWIK GARBOWSKI (*Ber.*, 1903, 36, 1215—1220. Compare this vol., ii, 299).—Different organic compounds readily yield colloidal gold solutions, even when the auric chloride solution employed has a concentration of 0.0001*N*. Platinic compounds yield colloidal solutions of platinum almost as readily, but with silver the reaction is much slower, and solutions of much higher concentration are required.

Phenol itself does not react so readily as dihydric and trihydric phenols; a 0.001*N* neutralised solution of auric chloride yields the coloured colloidal solution after some little time, whereas 0.0001*N* solutions of auric chloride, when mixed with 1—2 c.c. of 0.001*N* solutions of dihydric phenols, produce in a short time the characteristic colour. Pyrogallol acts somewhat more readily than phloroglucinol.

With platinic chloride and also silver nitrate solutions, resorcinol is less active than quinol and catechol.

Of the hydroxy-acids, salicylic, protocatechuic, gallic, tannic, and quinic acids, gallic acid is the most active, and with platinic salts is even more effective than pyrogallol; it yields green colloidal solutions of gold and platinum. Acetaldehyde, propaldehyde, and valeraldehyde, and also salicylaldehyde, yield colloidal solutions, but benzaldehyde does not. Vanillin produces blue solutions with auric chloride, and guaiacol also yields deep blue and then green solutions with alcoholic auric, and platinic chloride solutions.

J. J. S.

Volatility of Gold in presence of Zinc. K. FRIEDRICH (*Zeit. angew. Chem.*, 1903, 16, 269—271).—According to Hellot (Gmelin-Kraut, *Handbuch der anorg. Chem.*, 3, 1039), an alloy of 1 part of gold and 7 parts of zinc is entirely volatilised on being strongly heated. Grünhut (*Die Flamme*, 262) concludes that, during cremation, gold and zinc volatilise in appreciable quantities.

From experiments with alloys of gold and zinc, the author was unable to confirm Hellot's observation, and concludes that any loss of gold from the alloy is due to mechanical action of the gases present. Appreciable volatilisation of gold in presence of zinc can occur only when the latter is vaporised with great rapidity.

The loss of gold at temperatures up to 1500° is so slight that the conclusion may be drawn that even at higher temperatures the presence of zinc has no influence in promoting the volatility of gold.

A. McK.

Action of Sulphuric Acid on Platinum. JAMES T. CONROY (*J. Soc. Chem. Ind.*, 1903, 22, 465—468).—Below 200° , platinum is scarcely attacked by sulphuric acid, but at 250° the action is pronounced. Platinum dissolves in sulphuric acid to the extent of about 3000 grains per ton of acid. When greater than 92 per cent., the concentration of the acid has little influence on the rate of solution. Ammonium sulphate, ferrous sulphate, ferric sulphate, sodium chloride, and nitrates exert no influence on the rate of solution. Sodium arsenate and platinic chloride increase the solvent action, whilst carbon, arsenious oxide, sulphur, sulphur dioxide, and nitrous acid check the action. The influence of the last agents is probably due to their reducing character. The presence of reducing agents is beneficial in the concentrating of sulphuric acid in diminishing the solvent action on the platinum pans.

J. McC.

Mineralogical Chemistry.

Coorongite, a South Australian Elaterite. ALEX. C. CUMMING (*Proc. Roy. Soc. Victoria*, 1903, [N.S.], 15, 134—140).—Coorongite is found as a thin coating on the surface of the soil in the Coorong

district, South Australia. It is black and elastic, resembling caoutchouc. It contains 30 to 40 per cent. of mineral matter, mainly sand. About one-third of the organic matter is soluble in carbon disulphide; this soluble constituent is a clear, yellow, translucent, wax-like solid melting at 42° , and having the composition $C_{10}H_{18}O$ or $(C_{10}H_{18}O)_3$. The insoluble portion is a brown solid having the composition $C_{10}H_{20}O_3$. Intermediate oxidation products were obtained, and it is suggested that the substance is related to caoutchouc ($C_{10}H_{16}$), but is partly oxidised and hydrated.

L. J. S.

Berthierite from Bräunsdorf, Saxony. JOSEF LOCZKA (*Zeit. Kryst. Min.*, 1903, 37, 379—385).—Previous analyses show considerable variation owing to the presence of stibnite and pyrites in the material analysed. The results given under I were obtained after deducting 6.5 per cent. of quartz and 3.29 per cent. of pyrites. Analysis II is of material from which the stibnite had been extracted by digestion in an 8 per cent. solution of potassium hydrogen sulphide; this agrees closely with the formula FeS, Sb_2S_3 , which is probably the correct one for the mineral:

	S.	Sb.	As.	Fe,(Zn).	Cu.	Insol.	Total.
I.	28.72	[63.38]	trace	7.74	0.16	—	100.00
II.	29.36	54.69	trace	13.32*	0.10	1.30	98.77

Stibnite, when placed in potassium hydroxide solution, becomes red in colour, an oxysulphide being probably formed; the Bräunsdorf berthierite, when so treated, shows intimately intergrown stibnite.

L. J. S.

Cobalt Ores from New Caledonia. NICOLAI S. KURNAKOFF and N. PODKOPAJEFF (*Zeit. Kryst. Min.*, 1903, 37, 415; from *Verh. russ. min. Ges.*, 1902, 39, Prot. 15—17).—Analyses of asbolite from the Thia Louise mine gave:

	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	CoO.	NiO.	CuO.	MnO ₂ .	H ₂ O.	Total.
I.	2.80	41.20	12.52	0.30	0.20	4.05	1.63	—	20.77	18.74	102.21
II.	1.79	4.39	6.28	0.32	0.24	8.33	2.32	0.17	61.02	11.51	96.87

L. J. S.

Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XXX. The Isomorphous Mixtures Glaserite, Arkanite, Aphtalose, and Sodium Potassium Simonyite. JACOBUS H. VAN'T HOFF and H. BARSCHALL (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 359—371).—Neither potassium nor sodium sulphate, when crystallising in the rhombic modification from solutions containing them both in varying proportions, carries down any appreciable quantity of the other sulphate. From solutions of intermediate composition, however, another—a hexagonal—modification is formed, composed of both sodium and potassium sulphates in varying proportions, the limits of which lie between 77 and 62 per cent. of

* Zn, Mn = about 6.13 per cent.

potassium sulphate; these limits also include the natural minerals aphtalite, with 75 per cent. of potassium sulphate, and arkanite, with 62 per cent. of potassium sulphate.

To ascertain whether glaserite is an isomorphous mixture, saturated solutions were prepared at 60° with, on the one hand, potassium sulphate and glaserite, and, on the other, the isomorphous mixture of the two sulphates and sodium sulphate as "equilibrators" ("Bodenkörper;") Compare E. F. Armstrong, B.A. Report, 1901, 262), and that intermediate solution sought which was in equilibrium with glaserite and with the isomorphous mixture.

These solutions have the composition :

	Mols. in 1000 mols. water.	
	K ₂ SO ₄ .	Na ₂ SO ₄ .
K ₂ SO ₄ and glaserite.....	18·4	10·4
Isomorphous mixture and Na ₂ SO ₄ ...	13	53·7

It was not possible to obtain an intermediate solution of constant composition, accordingly glaserite is an isomorphous mixture, its formula being (1·33K, 0·67Na)SO₄.

Crystallographic investigations showed that a continuous series of isomorphous mixtures exists from glaserite, with 78·6 per cent. K₂SO₄, to arkanite, with 61·8 per cent. K₂SO₄, during which change the angle (10 $\bar{1}$ 1):(0001) increases from 56° to 59°.

A similar case of isomorphism is proved to exist in simonyite (sodium magnesium sulphate), where the sodium is partly replaced by potassium forming sodium potassium simonyite minerals, and leonite is shown to be really an isomorphous mixture having the formula Mg(1·52K 0·48Na)(SO₄)₂·4H₂O. E. F. A.

Alunogen from the Neighbourhood of Rome. FEDERICO MILLOSEVICH (*Zeit. Kryst. Min.*, 1903, 37, 395; from *Boll. Soc. Geol. Ital.*, 1901, 20, 263—270).—The walls of a cavern at Magagnano, near Viterbo, are encrusted with white to greyish-white alunogen. The mineral forms thin and small lamellar aggregates with pearly lustre, and is completely soluble in water. The following analysis agrees with the formula Al₂(SO₄)₃·16H₂O :

Al ₂ O ₃ .	Fe ₂ O ₃ .	SO ₃ .	H ₂ O.	Total.
16·02	trace	37·34	46·48	99·84

The mineral has probably been formed by the action of carbon dioxide and sulphuric acid (produced by the oxidation of hydrogen sulphide) on the felspar of the tuff which forms the walls of the cavern. Aluminium sulphate was obtained experimentally by the prolonged action of hydrogen sulphide, in the presence of air, on kaolin. L. J. S.

Scheelite from Sardinia. G. B. TRAVERSO (*Zeit. Kryst. Min.*, 1903, 37, 396; from *Riesocconti delle Riunioni d. Soc. Mineraria Sarda*, Iglesias, 1901, 6, 8—9).—Scheelite occurs with calcite and quartz as

small, lenticular masses in antimony ore at Villa Salto. Analyses of impure material are given. L. J. S.

Kedabekite and Violaite. EVGRAF STEPANOVICH FEDOROV (*Zeit. Kryst. Min.*, 1903, 37, 414; from *Ann. Inst. agron. Moscou*, 1901, 7, 43—47).—The name kedabekite is given to a dyke-rock from the Kedabek copper-mine, Caucasus; the rock consists of basic plagioclase (anal. III and IV), aplome (anal. V), and a pyroxene (anal. I and II). For the pyroxene, the name violaite is proposed; it is strongly pleochroic, with green to orange-yellow colours; extinction angle, $52\frac{1}{2}$ — $56\frac{1}{2}^\circ$.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.
I.	48.26	3.84	1.15	—	15.77	22.61	8.09	0.28	—
II.	48.14	4.93	1.23	—	14.45	22.96	7.99	0.30	—
III.	46.30	33.34	0.99	—	—	17.43	0.15	1.67	0.12
IV.	46.33	33.22	1.30	—	—	17.23	0.10	1.68	0.14
V.	39.16	9.25	16.73	0.51	4.01	28.71	1.75	0.34	0.03

L. J. S.

Composition of Axinite. W. E. FORD (*Amer. J. Sci.*, 1903, [iv], 15, 195—201).—The following analyses of axinite were made with a view to establishing a formula for the mineral, previous analyses having led to different results and different interpretations. I, crystals of excellent quality from Bourg d'Oisans, Dauphiné; II, material from Obira, Bungo, Japan.

	SiO ₂ .	B ₂ O ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
I.	42.78	6.12	17.67	0.99	6.02	2.99	20.16	2.41	1.40	100.54	3.287
II.	41.80	5.61	17.15	1.11	2.84	10.71	19.51	0.21	1.22	100.16	3.028

The new formula deduced from these analyses is expressed as an orthosilicate, $R''_7R''_4B_2(SiO_4)_8$; the small amount of water, only expelled at a high temperature, is present as basic hydrogen replacing the bivalent bases. Some previous analyses are discussed and shown to agree with the new formula.

A crystallographic description is given of the yellowish-brown axinite from Japan. L. J. S.

Hudsonite, an Amphibole, not a Pyroxene. SAMUEL WEIDMAN (*Amer. J. Sci.*, 1903, [iv], 15, 227—232).—A re-examination of the original hudsonite from Cornwall, New York, shows it to be an amphibole, and not a pyroxene as previously supposed. It has the cleavage angle and optical characters of amphibole, but is remarkable in possessing a pronounced parting parallel to the basal plane. Analysis by J. L. Nelson and W. W. Daniells gave:

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.
36.86	1.04	12.10	7.41	23.35	0.77	10.59
MgO.	Na ₂ O.	K ₂ O.	H ₂ O at 110°.	H ₂ O at red heat.	Total.	
1.90	3.20	1.20	0.70	0.60	99.72	

Hudsonite is closely related to barkevikite, hastingsite, and other alkali-amphiboles, which may perhaps be classed together under arfvedsonite.

L. J. S.

Physiological Chemistry.

Immunity of Fundulus Eggs and Embryos to Electrical Stimulation. ORVILLE H. BROWN (*Amer. J. Physiol.*, 1903, 9, 111—115).—The eggs of the small fish *Fundulus* are immune to electrical currents, as they are to osmotic changes in the surrounding medium. This is regarded as a physiological confirmation of the theory of the osmotic nature of electrolysis. The egg-membrane appears to be so freely permeable to ions that no polarisation can occur. The eggs of *Arbacia* and *Asterias* are susceptible both to currents and osmotic changes. As the *Fundulus* egg develops, there is a gradual increase in susceptibility to both kinds of change. Galvanotropic reactions depend primarily on the nervous system. The liquefaction of the eggs on the anode side, and the quieting effect of the cathode, supports Mathews' hypothesis of the dissolving action of the cations and their inhibitory action.

W. D. H.

Action of Chloroform, Ether, Alcohol, and Acetone on the Excised Mammalian Heart. FRANCIS W. TUNNICLIFFE and OTTO ROSENHEIM (*Proc. Physiol. Soc.*, 1903, xv—xvi; *J. Physiol.*, 29).—The action of these reagents on the heart was determined by adding them to saline fluid perfused through the heart by Locke's method. The depressing action on the heart produced by chloroform is very marked, but if lecithin is added also the effect is delayed. The quantity which seriously affects the heart is practically identical with that in the blood in fully narcotised animals. The amount of ether equal to that in the blood of animals narcotised by that reagent does not affect the heart seriously; the action of alcohol and acetone is insignificant.

W. D. H.

Action of Chloroform on the Heart and Blood-vessels. EDWARD ALBERT SCHÄFER and HERBERT J. SCHARLIEB (*Proc. Physiol. Soc.*, 1903, xvii—xix; *J. Physiol.*, 29).—The specific nature of the action of the drug on cardiac muscle is insisted on. The state of the heart called paralytic dilatation is regarded as one of excitatory inhibition; excitation of the terminal inhibitory mechanism is, however, distinguished from excitation of the vagus nerve and its endings, and can be brought about by chloroform when the vagus endings are thrown out of action by atropine. The high development of the inhibitory mechanism in the heart explains why it, of all muscular tissues, should be most profoundly affected. In the frog, chloroform produces contraction of blood-vessels, not dilatation as most observers

have stated ; in the frogs used, the central nervous system was destroyed either entirely or with the exception of the cerebrum. W. D. H.

Influence of Chemical Combination of an Element on the Rapidity of its Passage into the Blood. ANTOINE MOUNEYRAT (*Compt. rend.*, 1903, 136, 832).—It is well known that mercuric chloride is more toxic than mercurisuccinimide, and sodium arsenate than sodium cacodylate, even though the actual amount of the poisonous element be the same in both cases. In the present experiments, the substances were given hypodermically, and it was found that dogs which had received arsenic in mineral form (sodium arsenite or arsenate) have twice as much arsenic in their blood as those which have received a corresponding dose of arsenic in organic form (sodium methylarsinate). W. D. H.

Existence of Glycerol in Normal Blood. MAURICE NICLOUX (*Compt. rend.*, 1903, 136, 764—767).—The blood of the dog and rabbit contains minute quantities of glycerol. The physiological significance of this and of the variations in the amount of glycerol will form the subject of future work. W. D. H.

The Gastric Juice of Newly-born Animals. OTTO COHNHEIM and FRANZ SOETBEER (*Zeit. physiol. Chem.*, 1903, 37, 467—474).—The experiments show that in newly-born dogs the secretion of gastric juice is reflex, in which the act of sucking and appetite ("psychical juice") are important factors. Even on the first day of life, the juice contains hydrochloric acid ; lactic acid is absent. The presence of ferments could not, however, be proved at this early stage. W. D. H.

Precipitability of Pancreatic Ferments by Alcohol. HORACE M. VERNON (*J. Physiol.*, 1903, 29, 302—334).—The amount of ferment thrown down by adding alcohol to glycerol extracts of pancreas increases regularly with the amount of alcohol added ; the precipitability of the diastatic ferment is much less than that of the tryptic ferment. The diastatic ferment is, however, destroyed to a great extent in the processes of precipitation and resolution. The destruction of the ferment is increased by the addition of more glycerol. It was not possible to separate the tryptic and rennetic ferments by fractional precipitation with alcohol ; it is suggested that they are not separate entities, but form a complex group, of which various side-chains possess different powers. The connection between proteolytic and rennetic activity is close in many ferments, the latter action being sometimes accidental and occurring where any possibility of acting on milk is absent. Zymogens and enzymes cannot be separated by the alcohol method. The same is true for trypsin of varying degrees of stability. W. D. H.

Uracil from Autolysis of the Pancreas. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1903, 37, 527—529).—On autolysis of the pancreas, uracil is obtained as one product, but no thymine. In

the hydrolysis of the nucleic acid of the pancreas, only thymine is obtained. It is probable that a change of one substance into the other occurs.

W. D. H.

Lipolytic Actions. HENRI POTTEVIN (*Compt. rend.*, 1903, 136, 767—769).—The fat which enters the blood by the stream of chyle rapidly disappears; doubt, however, has been cast on the existence in the blood of a lipolytic ferment. The present experiments show that the addition of blood-serum intensifies the action of pancreatic extracts on fats; the same occurs when the serum has been previously acidified, boiled, and filtered. The action is attributed to the salts of the serum, and is regarded as an instance of the importance of ionic action on ferment activity. If the fat is simply agitated with pancreatic juice or extract, and then thoroughly washed, it rapidly undergoes saponification when suspended in serum. It is suggested that the fat which enters the circulation has in a similar way sufficient of the pancreatic steapsin attached to it to bring about saponification in the fat in the blood stream.

W. D. H.

Autolysis of Lymph Glands. ALFRED REH (*Beitr. chem. Physiol. Path.*, 1903, 3, 569—573).—The decomposition products found as the result of the autolysis of lymph glands, were ammonia, leucine, tyrosine, thymine, and uracil.

W. D. H.

Autolysis of Leucæmic Spleen. OTTO SCHUMM (*Beitr. chem. Physiol. Path.*, 1903, 3, 576—579).—On autolysis of a leucæmic spleen, the large amount of proteose which it contained diminished; simple substances such as lysine, leucine, tyrosine, and ammonia are formed. Aspartic acid, glutamic acid, and thymine were not found. The amount of hydrolytic products formed is much greater than the amount of proteose which disappears; they must therefore, in great measure, arise from the coagulable proteids of the spleen. On autolysis of a spleen from a case of perityphlitis, the amount of non-coagulable nitrogenous products obtained was nearly as great as from the leucæmic spleen.

W. D. H.

Organic Phosphorus Compounds and Nutrition. F. BILLON and HENRI STASSANO (*Compt. rend. Soc. Biol.*, 1903, 55, 276, 277—279).—In view of the statements of Danilewsky on the stimulating influence of lecithin, experiments were undertaken in which young rabbits of the same litter were fed in the same way, except that some also received lecithin, others nucleic acid, and others sodium methylphosphinate. Those which had the lecithin, increased in weight most rapidly, nucleic acid produced the next best effect, then sodium methylphosphinate. Two experiments only are given, and in one of these the effect is not very striking.

W. D. H.

Perfusion of Surviving Organs. THOMAS GREGOR BRODIE (*J. Physiol.*, 1903, 29, 266—275).—A new apparatus is described and figured by means of which blood can be perfused through isolated organs and be properly aerated before it returns to the organ. The

defibrinated blood of the animal itself is the best to use for most purposes.
W. D. H.

Formation of Glycogen in Perfused Liver. KARL GRUBE (*J. Physiol.*, 1903, 29, 276—281).—Using Brodie's apparatus (preceding abstract), the liver is shown to retain for some time after isolation from the body the power of forming glycogen from dextrose. The liver is very sensitive to interferences with its circulation; cessation of the blood flow even for a few minutes produces harmful effects on the liver cells, causing them to effect the transformation of stored glycogen into sugar. To avoid this, it is imperative that the operative procedure is done rapidly, and that the organ be not removed from the body; the artificially pumped blood is led to the splenic vein and the blood made to flow into the liver immediately its normal supply from other sources is cut off. Further experiments are in progress.
W. D. H.

Coagulation of Muscle Plasma. OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1903, 3, 543—568).—Search for a special "rigor ferment" yielded negative results; extracts of rigored muscle, or the juice expressed from muscle after rigor, or after autolysis, produced on injection no acceleration of rigor in an animal just killed; or if acceleration occurs, it occurs equally well after the fluid has been boiled and filtered. The hypothetical ferment does not exist either in the form of zymogen. Various reagents produce acceleration of the onset, delay, and disappearance, of *rigor mortis*, but no evidence that this is due to a ferment was found. Experiments designed to prove that the acid formed during rigor is responsible for the onset and disappearance of rigor also yielded negative results. The acid formed appears to be, undoubtedly, paralactic acid. Calcium salts accelerate the coagulation of muscle plasma, but are not indispensable.
W. D. H.

Formation of Glycogen from Glyco-proteids. LYMAN BRUMBAUGH STOOKEY (*Amer. J. Physiol.*, 1903, 9, 138—146).—Experiments on hens rendered as free as possible from glycogen by starvation are described; their object was to settle the question whether glycogen formation from proteids only occurs when gluco-proteids are given. The main difficulty of arriving at a conclusion is due to the fact that the amount of residual glycogen after starvation is uncertain. So far as any conclusion can be drawn from the experiments described, glycogen appears to be formed from proteids whether they contain a carbohydrate radicle or not.
W. D. H.

Nucleo-proteid of the Liver. J. WOHLGEMUTH (*Zeit. physiol. Chem.*, 1903, 37, 475—483).—According to Halliburton, the percentage of phosphorus in the nucleo-proteid of the liver is 1.45. Using methods similar to those employed by Hammarsten in his investigations on the nucleo-proteid of the pancreas, the product obtained in the present research contained 2.98 per cent. of phosphorus. Halliburton's substance is regarded as a decomposition product of this more complex

nucleo-proteid. The sugar obtained from liver nucleo-proteid is *l*-xylose.
W. D. H.

Oxydases in Cuttle-fish. C. GESSARD (*Compt. rend.*, 1903, 136, 631—632).—The ink-sac of a cuttle-fish was found to contain tyrosinase, laccase, and an oxidising diastase of another kind which is more resistant to heat than laccase.
N. H. J. M.

Inorganic Constituents of Medusæ. A. B. MACALLUM (*J. Physiol.*, 1903, 29, 213—241).—From observations on *Aurelia* and *Cyanea*, the following conclusions are drawn: their salinity as indicated by the total amount of halogen is usually different from that of the sea-water they live in, and is different in the two forms, although taken from the same sea-water on the same day. If the composition of the water varies in the 24 hours through tidal currents, the salinity of *Aurelia* remains practically unchanged. The sodium is slightly less, and the potassium much more, than in the water, the calcium is about the same as in the water, the magnesium less (down to 10 per cent. less), and the deficiency in sulphuric acid may reach 36 per cent. Such facts point to selective action in the cells lining the gastrovascular channels, and also in those covering the organisms. The different selective power towards various constituents is explained by reference to the geological history of those constituents in the ocean, and the inorganic composition of the jelly-fish reflects to a certain extent the composition of sea-water, not only of to-day, but of past and remote epochs. Iron is more abundant, and iodine less so than in sea-water. The iodine is not associated with any compound precipitable by alcohol. Many of Loeb's theories are combated.
W. D. H.

Action of Acid and of Chloral on the Secretion of Bile. E. WERTHEIMER (*Compt. rend. Soc. Biol.*, 1903, 55, 286—287).—Injection of acid into the upper part of the intestine, but not into the lower part, produces an increased flow of bile. If the pneumogastric and sympathetic nerves were cut, the same result occurred in five out of 12 experiments. Complete denervation of the viscera has not been performed. Chloral, on the other hand, acts as a cholagogue, even if it is introduced per rectum, and therefore probably after absorption.

W. D. H.

Acidity of Urine. RUDOLF HÖBER (*Beitr. chem. Physiol. Path.*, 1903, 3, 525—542).—Two forms of acidity are distinguished: (1) that which depends on the relation between dissociated and undissociated hydrogen, which is united to hydroxyl; this is termed titration acidity; for the determination of this, phenolphthalein is regarded as the best indicator; and (2) that which depends on the concentration of dissociated hydrogen; this is termed ionic acidity and is best determined by an electrical method described in full. There is no parallelism between the two forms.
W. D. H.

Ammonia in the Urine. GEORG LANDSBERG (*Zeit. physiol. Chem.*, 1903, 37, 457—459).—Schwarz (*Wien. Med. Woch.*, 1893, No. 3) stated that the amount of ammonia in the urine as usually given is too high, and that if decomposition of the urine is prevented by chloroform, the normal amount of ammonia per diem averages 0.15 instead of 0.7 gram. In the present research, the mean found in eight specimens was 0.57; the addition of chloroform makes no difference.

W. D. H.

Excretion of Bromal Hydrate in the Urine. GUGLIELMO MARALDI (*Chem. Centr.*, 1903, i, 781; from *Boll. Chim. Farm.*, 42, 81—85).—Bromal is excreted in the urine exclusively as urobromalic acid; this is analogous to the behaviour of chloral.

W. D. H.

Influence of Quinic Acid on Hippuric Acid Excretion. FRZ. HUPFER (*Zeit. physiol. Chem.*, 1903, 37, 302—323).—The subject of the "grape cure" and similar cures is discussed in relation to the treatment of gout. From experiments on the author's own person, he concludes that the administration of such fruit in large quantities has very little influence on the excretion of uric and hippuric acids, and certainly there is no inverse relation of the proportions in which these substances are excreted. Quinic acid and its salts, on the other hand, greatly increase the excretion of hippuric acid; there is also a slight rise in the amount of uric acid excreted.

W. D. H.

Physiological Action of Sodium Bromovalerate. CH. FÉRÉ (*Compt. rend. Soc. Biol.*, 1903, 55, 279—281).—This antispasmodic remedy lessens the amount of work done and hastens the onset of fatigue, as tested by Mosso's ergograph.

W. D. H.

Action of Suprarenal Extract. S. J. MELTZER and CLARA MELTZER (*Amer. J. Physiol.*, 1903, 9, 147—160).—Some evidence is adduced to show that the vaso-constricting effect of suprarenal extract is in part due to its action on the vaso-motor centre, and that it also stimulates vaso-dilatators.

W. D. H.

Intravascular Injection of Animal Extracts. SWALE VINCENT and WILLIAM SHEEN (*J. Physiol.*, 1903, 29, 242—265).—Extracts of nervous tissues contain a depressor substance which the author still considers is not choline. There is distinct evidence also that a pressor substance is present, especially in extracts made with cold saline solution, and which therefore contain proteid. The same is true for extracts of muscle and of kidney. Liver, spleen, pancreas, intestine, lung, testis, ovary, thyroid, thymus, suprarenal, and pituitary also contain a depressor substance. The suggestion of Bayliss and Starling that the products of certain tissues will be found to act as vaso-dilatators only or specially for certain tissues in functional relation to those in which they arise is not agreed with. The chemical nature of the substances in question is not discussed, and their normal function is left undetermined.

W. D. H.

Nephrotoxins. H. BIERRY (*Compt. rend.*, 1903, 136, 909—910).—Repeated injections into the rabbit, not only of kidney cells from the dog, but also of certain chemical constituents (nucleo-proteid in nature) of those cells, provoke the appearance in the rabbit's blood of a substance, nephrotoxin, which is most harmful to the kidney cells of the dog. W. D. H.

Influence of Cold on the Action of some Hæmolytic Agents. GEORGE N. STEWART (*Amer. J. Physiol.*, 1903, 9, 72—96).—At 0°, the laking action of sapotoxin is retarded, and before the hæmoglobin is liberated the conductivity of the blood is increased, owing to an increase in the permeability of the envelopes to electrolytes. Bile salts produce this less distinctly, foreign serum not at all. The action of sapotoxin is in three stages: (1) an action on the envelope which does not necessarily or immediately cause liberation of hæmoglobin, (2) an action on the hæmoglobin or the stroma that produces a discharge of the pigment, and (3) an action on the stroma causing a setting free of electrolytes. W. D. H.

Irritability of the Brain during Anæmia. WILLIAM J. GIES (*Amer. J. Physiol.*, 1903, 9, 132—137).—The functions of the brain soon cease if it is rendered anæmic by perfusion of serum or Ringer's fluid. Convulsions only take place when the anæmia is induced rapidly. If the anæmia is gradually produced, the functions in cold-blooded animals cease in the following order: respiration, skin reflex, lid reflex, nose reflex, heart beat. In warm-blooded animals, the order is lid reflex, respiration, nose reflex, heart beat. W. D. H.

Cretinism in Calves. C. G. SELIGMANN (*Proc. Physiol. Soc.*, 1903, ix—x; *J. Physiol.*, 29).—Cretinism occurs in calves of the Dexter-Kerry breed. It is associated with malformation and absence of colloid substance in the thyroid, and probably arises primarily from placental disease. W. D. H.

Intravascular use of Antiseptics. W. V. SHAW (*J. Hygiene*, 1903, 3, 159—165).—The use of antiseptics injected into the blood has been recommended in tubercle and other diseases, but has seldom yielded positively beneficial results. The present experiments conducted on rabbits poisoned with *Bacillus pyocyaneus*, and treated with formalin and other substances intravenously, show that there are no advantages to be derived from this method of treatment. W. D. H.

Adrenalin Glycosuria. DIARMID NOËL PATON (*J. Physiol.*, 1903, 29, 286—301).—The subcutaneous administration of adrenalin in dogs and rabbits produces true glycosuria and glycaemia, the degree of which depends largely on the previous carbohydrate store in the body, but which occurs also when this store is exhausted. It is apparently due to a lessened utilisation of sugar in the tissues, and not to an increased formation or excretion of sugar. It is much more marked than glycosuria, which results from lessened processes of oxidation. The toxic action of adrenalin is probably not direct, but indirectly through an

effect on the pancreas. A distinct tolerance of the drug is established after a time, and days may occur when sugar is absent from the urine. The urine gives a dark red ring with nitric acid, but acetoacetic acid and acetone were not detected. Proteid metabolism goes on as in ordinary diabetes; the sugar is not wholly derived from the breaking down of proteid, although on an insufficient diet the decomposition of proteid is increased, but proteid absorption is unaffected; ammonia is markedly increased.

W. D. H.

Glycuronic Acid in Icteric Urine. E. C. VAN LEERSUM (*Beitr. chem. Physiol. Path.*, 1903, 3, 574—576).—Bile having been shown to contain glycuronic acid, it became necessary to search for that acid in the urine in cases of jaundice. It was found to be present, and its presence will account for some of the reducing properties of icteric urine.

W. D. H.

Calculi from the Prostate. PUAUX (*J. Pharm. Chim.*, 1903, [vii], 17, 428—430).—A description and analysis of calculi removed from the prostate, which contained water, 9; calcium oxalate, 40; calcium carbonate, 8; calcium phosphate, 17; ammonium magnesium phosphate, 12; organic matter (probably uric acid) and potassium, 14 per cent.

G. D. L.

Analysis of a Liquid from a Pancreatic Cyst. J. ALAY and RISPAL (*J. Pharm. Chim.*, 1903, [vi], 17, 319—320).—The liquid is feebly alkaline, contains less albumin and urea, but more albumin soluble in acetic acid, than is usually the case in such liquids, and acetone. It contained per litre, total proteids, 8.7 grams (serin, 5.1; globulin, 0.6; albumin soluble in acetic acid, 3.0); NaCl, 5.8; P_2O_5 , 0.16; CaO and MgO, 0.05; urea, 0.14; fat and cholesterol, 0.16; acetone, about 0.05 gram; and traces of uric acid and sulphates.

G. D. L.

Distribution in the Organism and Elimination of Arsenic given as Sodium Methylarsinate. ANTOINE MOUNEYRAT (*Compt. rend.*, 1903, 136, 696—697).—Arsenic has no tendency to accumulate in the organs of the body, but it is practically all eliminated within thirty days after ingestion.

W. D. H.

Cobra Poison. PRESTON KYES and HANS SACHS (*Chem. Centr.*, 1903, i, 888; from *Berl. klin. Woch.*, 40, Nos. 2, 3, 4).—The lecithin of the stromata of the red corpuscles is regarded as the complement of cobra poison. Cholesterol inhibits the hæmolysis of this and other lysins, but in different degrees. Potassium permanganate, calcium chloride, gold chloride, and sodium hydroxide destroy cobra poison. Bile and milk, if first heated to 100°, increase its activity. Hydrochloric acid protects it from the destructive influence of high temperatures. Fatty acids, soaps, chloroform, and neutral fat are hæmolytic, and their action in this direction is increased by cobra poison.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation. J. H. ABERSON (*Rec. trav. chim.*, 1903, 22, 78—132).—The fermentative decomposition of dextrose takes place according to the equation $C_6H_{12}O_6 = 2EtOH + 2CO_2$. An experimental determination of the velocity of the reaction, using yeast, shows that the value of k calculated for a unimolecular reaction increases with the time. The mean velocity, however, is directly proportional to the quantity of yeast present. The dextrose exerts a retarding influence and, consequently, as this disappears by decomposition the speed is accelerated. Allowing for this retardation, a satisfactory constant is obtained for a unimolecular reaction. The influence of temperature on the reaction constant has been calculated by means of the Arrhenius formula, and it is found that temperature influences the fermentation to about the same extent as it does the majority of chemical reactions. Like dextrose, alcohol also exerts a retarding influence on the reaction, but not to such a great extent.

The reaction is one of equilibrium, and the influence of the quantity of yeast, the temperature, alcohol, carbon dioxide, and the concentration of the dextrose have been investigated. The quantity of yeast present is without influence on the final state of equilibrium. The effect of the preliminary addition of alcohol or carbon dioxide (added in the solid state) is to cause the equilibrium to be established much sooner than should be the case according to the law of mass action. If the concentration of the dextrose is very high, the decomposition does not proceed so far as if it is somewhat lower, and it is not possible to account for this by an increase of the osmotic pressure.

As the equilibrium is such that at 20° a greater decomposition has taken place than at 31°, ten experiments were made in order to find if any reversion takes place, and thus establish that the reaction is a reversible one. Sealed tubes containing dextrose and yeast were maintained at 20° until the equilibrium was established (24 hours); they were then placed in a bath at 31°. Only in two cases was it possible to detect any reversion, and the author does not think it is yet certain that the reaction is a truly reversible one. J. MCC.

Production of Formic Acid in Alcoholic Fermentation. PIERRE THOMAS (*Compt. rend.*, 1903, 136, 1015—1016).—When yeast is grown in a medium containing carbamide, a large quantity of formic acid is produced. The same takes place, but to a smaller extent, when the carbamide is replaced by acetamide, either alone or after the addition of ammonium hydrogen carbonate, sulphate, acetate, succinate, or aspartate. The addition of calcium carbonate to the culture causes an augmentation of the volatile acid formed.

Since many natural culture media, such as grape-juice, contain amides and ammonium salts, it is not surprising to find formic acid, as has been done by Rayman and Kruis and by Khoudabachian, in the

wine soon after fermentation. The production of formic acid in these cases diminishes as the amide becomes used up. J. McC.

Lactic Acid Fermentation. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1903, 37, 381—382).—By Buchner's method, a juice can be expressed from pure cultures of *Bacterium acidi lacti*, and the powder obtained by drying this is free from bacteria. It is able to convert lactose into lactic acid. W. D. H.

Natural Curdling of Milk. YOSHINAO KOZAI (*Bied. Centr.*, 1903, 32, 273—277; from *Zeit. Hyg. u. Inf.*, 1901, 38, 386).—The results of experiments with different samples of milk showed that when kept under conditions which permitted abundant access of air, lactic acid is almost always found in considerable quantity. In one case, in which the time had been more prolonged and the temperature higher, no lactic acid could be detected; a sample of the same milk, however, kept at the ordinary temperature, and for a shorter time, was found to contain much lactic acid. Succinic acid was sometimes present, but usually only in very small quantities. Two samples, in which lactic acid was absent, contained a large amount of succinic acid besides ammonia and trimethylamine. Acetic acid was frequently present in samples kept at the ordinary temperature, and was regularly produced in samples kept at a higher temperature. Butyric acid was sometimes, and alcohol frequently, found. Peptone occurred in samples in which the decomposition had not gone very far.

The nature of the lactic acid produced depends indirectly on the temperature, a lower temperature being favourable to the formation of *d*-lactic acid, and *vice versa*.

Of the lactic acid bacteria found in spontaneously curdled milk, *Bacillus acidi paralactici* (Leichmann's *Bact. lactis acidi*) was much the most prominent; *B. acidi lævolactici*, *Micrococcus acidi paralactici*, and *Bacterium coli* were also present. N. H. J. M.

Fermentative Fat-hydrolysis. KARL BRAUN and EMIL C. BEHRENDT (*Ber.*, 1903, 36, 1142—1145. Compare Green, *Proc. Roy. Soc.*, 1890, 48, 370; Siegmund, *Abstr.*, 1890, 1455; 1892, 1261; and Connstein, Hoyer, and Wartenberg, this vol., ii, 218).—The authors confirm the statement of Green and Siegmund (*loc. cit.*) in the case of the ferment of Jequirity seeds (*Abrus precatorius*), and that of Connstein, Hoyer, and Wartenburg (*loc. cit.*) with regard to the ferment of castor oil seeds. Castor oil is slowly hydrolysed by the emulsin of sweet almonds, but not by preparations of bearberry leaves (*Arctostaphylos uva ursi*). T. A. H.

Assimilation of Sterigmatocystis Nigra. HENRI COUPIN (*Compt. rend. Soc. Biol.*, 1903, 55, 329—330, 357—358, 406—408).—Raulin has shown that magnesium is indispensable for the nutrition of this mould; he used it in the form of the carbonate. In the present research, eight other salts of magnesium were found to act equally well. In the same way, ammonium phosphate is not the only phosphorus

compound which is available; of eight compounds, sodium hypophosphite was the only one not utilisable. As regards sulphur, the effects are more variable; some compounds are poisonous, some indifferent; the most assimilable is ammonium sulphate. W. D. H.

Formation of Oxalic Acid by Moulds. OSKAR EMMERLING (*Centr. Bakt. Par.*, 1903, 10, 273—275. Compare *Abstr.*, 1902, ii, 521).—Oxalic acid is not formed by the growth of *Aspergillus niger* in solutions of carbohydrates, polyhydric alcohols, or acids other than amino-acids. Ammonium oxalate results in various proportions from the growth in aminoacetic acid, α -serine, alanine, aspartic acid, asparagine, glutamic acid, pyrrolidine-2-carboxylic acid, gelatin, casein, egg-albumin, and peptone, but not, in spite of growth of the mould, from hippuric acid, arginine, histidine, lysine, or glucosamine. In other instances quoted, there was no growth, and with phenylalanine only a slight growth, with corresponding formation of oxalate.

G. D. L.

Decomposition of Fodder and Foods by Micro-organisms.
IV. Decomposition of Vegetable Foods by Bacteria. JOSEF KÖNIG, ALB. SPIECKERMANN, and A. OLIG (*Zeit. Nahr. Genussm.*, 1903, 6, 241—258, and 289—296. Compare this vol., ii, 169).—Experiments with cotton-seed meal showed that, in the complete absence of air, bacteria of the type *Bacterium coli* developed most rapidly, sugar being fermented with the evolution of gases. *Cocci* were also present and caused acid fermentation of the sugar to take place without formation of gas. Under ordinary conditions, the acidity produced prevented the growth of pure anaërobic organisms. A considerable loss of organic matter accompanied the growth of the bacteria under anaërobic conditions, the loss being at first due to the destruction of carbohydrates. Afterwards, the proteids and pentosans were strongly attacked. The fat was only slightly altered. The bacteria which caused fermentation of the sugar to take place only decomposed the fat, pentosans, and proteids to a small extent; those which attacked the proteids of cotton-seed meal behaved similarly towards other animal and vegetable proteids. The following substances were found to be present in the decomposition products: albumoses, peptones, amino-bases, volatile fatty acids (butyric, valeric, &c.), aromatic acids (phenylacetic, phenylpropionic), succinic acid, scatolecarboxylic acid, aromatic hydroxy-acids, indole, scatole, phenol, ammonia, carbon dioxide, and volatile sulphur compounds. Ptomaines and other poisonous substances could not be detected.

W. P. S.

Action of Zinc on Microbes in Water. F. DIENERT (*Compt. rend.*, 1903, 136, 707—708).—If metallic zinc is added to water containing micro-organisms (Eberth's bacillus and *Pacillus coli*), in thirty-six hours the surface portion of the water is sterile; the organisms are all in the deeper portions near the zinc. This they attack, and the zinc salts so formed in time kill the bacteria. W. D. H.

Nitrification. GEORGE S. FRAPS (*Amer. Chem. J.*, 1903, 29, 225—241).—The number of nitrifying organisms in a soil varies according to conditions. The intensity of nitrification varies considerably, being very slight during the periods in which the organisms multiply. In the case of sterilised nitrogenous soil inoculated with nitrifying organisms, the intensity of nitrification increased, on the whole, with the duration of the experiment; the nitrifying organisms probably multiply continuously, and there are periods in which nitrification is greatly diminished.

The differences in the rate of nitrification of cotton-seed meal and of ammonium sulphate is due to the existence of two groups of nitrifying organisms in soils. The relative number of either group may be increased by growing in soil containing ammonium sulphate or cotton-seed meal.

In addition to the three groups of organisms which produce successively from organic matter ammonium salts, nitrites, and nitrates, there is a fourth group which converts organic matter into nitrites or nitrates.
N. H. J. M.

Presence of an Erepsin in Basidiomycetes. C. DELEZENNE and H. MOUTON (*Compt. rend.*, 1903, 136, 633—635. Compare this vol., ii, 229).—The experiments were made with *Amanita muscaria*, *A. citrina*, *Psalliota campestris*, and *Hypholoma fasciculare*, and others. One gram of the substance in 20 c.c. of water and about 0.5 gram of gastric peptone caused the biuret reaction to disappear in four or five days.

In some cases, when kinase was present only in very small quantity, the erepsin was very active. There can be no doubt as to the individuality of the two diastases (compare Hamburger and Hekma, *J. Phys. Path. Gén.*, 1902).
N. H. J. M.

Wax of Flax. CAMILL HOFFMEISTER (*Ber.*, 1903, 36, 1047—1054).—A wax can be extracted by ether or petroleum from flax threads and is deposited from these solvents in grains of an indistinct, crystalline structure melting at 61.5° and having a sp. gr. 0.9083 at 15°, insoluble in water, partially soluble in alcohol, and sparingly so in chloroform. This wax can be easily obtained in quantity from the "flax-dust" of the spinning-house, of which it forms 10 per cent. It has the following characters: non-hydrolysable material, 81.32 per cent.; acid number, 54.49; saponification number, 101.51; ether number, 49.54; Reichert-Meissl number, 9.27; iodine number, 9.607; and Hehner's number, 98.31.

The hydrolysable material yielded fatty acids, which were separated into solid acids and liquid acids by extracting the mixture of their lead salts with ether. The solid acids were a mixture of palmitic acid together with a small quantity of stearic acid, and were separated by fractional precipitation of their alcoholic solution with barium acetate. In order to separate the liquid unsaturated acids, they were oxidised with permanganate and their oxidation products severally isolated; thus, the presence of oleic, linolic, and the two linolenic acids was demonstrated.

The non-hydrolysable material was heated with acetic anhydride, when the major portion remained untouched. It consisted mainly of a paraffin-like material, ceresin, which melted at 68° , and had a sp. gr. 0.9941 at 10° .

The acetyl derivatives, which were dissolved in the acetic anhydride, were allowed to crystallise in two fractions; the first which separated was the acetyl derivative of cholesterol or phytosterol; the second fraction was ceryl acetate (m. p. 64.3°). K. J. P. O.

Decomposition and Regeneration of Proteids in Plants. GABRIELLE BALICKA-IWANOWSKA (*Bull. Acad. Sci. Cracow*, 1903, 9—32).—The asparagine formed during the decomposition of proteids is a secondary product, the primary products being amino-acids and hexon-bases. The regeneration of proteids from their products of decomposition is influenced by mineral salts, and a deficiency of calcium is the chief cause of the diminution of the amount of proteid formed. Assimilation influences the regeneration of proteids, but light seems also to have a direct action. N. H. J. M.

Effect of Moisture on the Availability of Dehydrated Aluminium Phosphate. FRED. W. MORSE (*J. Amer. Chem. Soc.*, 1903, 25, 280—288).—A large number of experiments showing that in the dehydration of aluminium phosphate (Redonda phosphate) the temperature need not be carefully kept at 325° , but may safely reach the melting point of borax (560°); a higher temperature, however, is injurious.

Reabsorption of moisture seriously affects the solubility of the samples in ammonium citrate and lessens their value. L. DE K.

Analytical Chemistry.

Detection of Hydrogen Peroxide in Milk. CARL ARNOLD and CURT MENTZEL (*Zeit. Nahr. Genussm.*, 1903, 6, 305—309).—Hydrogen peroxide may be detected in either raw or heated milk, to which it is sometimes added as a preservative by mixing 10 c.c. of the milk with 10 drops of a 1 per cent. solution of vanadic acid in dilute sulphuric acid. The presence of 0.01 gram of hydrogen peroxide in 100 c.c. of milk causes a red coloration to appear. By using titanous acid instead of vanadic acid, a yellow coloration is obtained. The *p*-phenylenediamine test is the most sensitive, but it is only applicable directly in the case of raw milk. In testing heated milk with *p*-phenylenediamine, a little raw milk must be added to supply the oxydase necessary for the reaction. Samples of milk should be tested as soon as possible after being received, as hydrogen peroxide decomposes somewhat rapidly. W. P. S.

Estimation of Chlorine in Animal Secretions, Organs, Foods, &c. CASIMIR STRYZYKOWSKI (*Chem. Centr.*, 1903, i, 601; from *Oesterr. Chem. Zeit.*, 6, 25—28).—Ten c.c. of the liquid to be tested, or 10 grams of the solid matter suspended in water, are mixed with 1 gram of pure magnesium oxide, evaporated to dryness in a platinum dish, and finally ignited to burn off the carbon. The ash is dissolved in water containing sufficient sulphuric acid to neutralise the magnesium oxide, the unavoidable excess of acid neutralised with calcium carbonate, and the chlorine titrated with standard silver solution.

L. DE K.

Estimation of Iodides when Mixed with other Salts. CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1903, 42, 163—167).—The iodine of the iodide is set free by potassium dichromate and hydrochloric acid; the mixture is then shaken with chloroform, which takes up the iodine, and this, after removal of the aqueous liquid, is titrated by sodium thiosulphate in presence of an aqueous solution of potassium iodide.

The chloroform should be as free as possible from alcohol, and the titration should be performed without adding any acid. Chlorides, nitrates, and free acids have no influence on the result, but bromides are slowly oxidised by the acid chromate, and must therefore be absent. Any substances soluble in chloroform may first be removed by shaking with that solvent, since iodides are not removed by it from an aqueous solution.

M. J. S.

Iodometric Standardisation. HUGO DITZ and B. M. MARGOSCHES (*Zeit. angew. Chem.*, 1903, 16, 317—321).—The process for the estimation of chlorates (Abstr., 1901, ii, 687) may be used in turn for the standardisation of sodium thiosulphate solution.

A weighed quantity of potassium chlorate dissolved in water is put into the apparatus previously described and decomposed with potassium bromide and concentrated hydrochloric acid. After largely diluting with water, the liberated bromine is treated with potassium iodide, when a definite weight of free iodine will be obtained, with which the thiosulphate is at once standardised.

L. DE K.

Estimation of Sulphur in Pig-iron. CLARENCE A. SEYLER (*Analyst*, 1903, 28, 97—101).—By heating the sample in a porcelain crucible to 750° after covering it with a layer of filter-paper to provide a non-oxidising atmosphere, results were obtained, on applying the evolution method, nearly equal to those of the oxidation process. In the evolution method, the use of concentrated hydrochloric acid is recommended, together with an absorbent, for the gases, consisting of bromine and hydrochloric acid. Absorption by potassium hydroxide leads to low results. Passage of the gas, mixed with hydrogen, through a red-hot tube gives good results if concentrated hydrochloric acid be used.

W. P. S.

Quantitative Separation of Sulphides and Haloids. WILHELM BILTZ (*Zeit. anal. Chem.*, 1903, 42, 159—163).—The solution is precipitated with an excess of silver nitrate, and is then feebly acidified with nitric acid. After washing from the excess of silver nitrate, the precipitate is digested in the cold with a feebly ammoniacal 50 per cent. solution of sodium thiosulphate, and after partially washing the undissolved silver sulphide with the same cold solution, the washing is completed with hot thiosulphate. Silver chloride, bromide, and iodide are completely dissolved, and are estimated by precipitating the silver from the thiosulphate solution by addition of ammonium sulphide.

M. J. S.

Gas Analysis in Flasks. III. ALFRED WOHL (*Ber.*, 1903, 36, 1417—1422).—The principle of the method adopted by Wohl and Poppenberg (this vol., ii, 328) for estimating the nitrogen in nitrates is applied to the estimation of ammonia by the sodium hypobromite method, and the determination of carbon dioxide in solid carbonates. Analyses are given showing the accuracy of the method.

W. A. D.

Ammoniacal Citrate Solution as used in the Estimation of Phosphoric Acid. A. VERWEIJ (*Zeit. anal. Chem.*, 1903, 42, 167—168).—Citrate solutions which have been kept for some months frequently give too high a result when used for the analysis of superphosphate, &c. This seems to be due to the presence of silica, which the citrate solution dissolves from certain varieties of glass.

M. J. S.

Decomposition of Insoluble Calcium Phosphates by Ammonium Citrate Solutions. KARL ZULKOWSKI and FRANZ CEDIVODA (*Chem. Centr.*, 1903, i, 477—478; from *Chem. Ind.*, 26, 1—9).—The original paper contains a description of experiments and other details from which the following conclusions are drawn. The solution of insoluble calcium phosphates by ammonium citrate solution depends on the formation of normal and acid calcium ammonium citrates of which the latter alone are stable. Dicalcium ammonium dicitrate is rather sparingly soluble, and its solution quickly decomposes, forming insoluble tricalcium dicitrate and triammonium citrate. Calcium tetrammonium dicitrate, on the other hand, is readily soluble, but gradually dissociates, forming first dicalcium ammonium dicitrate and then tricalcium dicitrate and triammonium citrate. Dicalcium phosphate is dissolved by triammonium citrate, diammonium citrate, or monoammonium citrate. In the first case, a large excess of the citrate is required, ammonium hydrogen phosphate and normal calcium tetrammonium dicitrate being formed by a reversible reaction, whilst in the second and third cases, ammonium hydrogen phosphate and calcium ammonium dicitrate, and monocalcium phosphate and calcium ammonium dicitrate are formed respectively. Dicalcium phosphate is completely dissolved by the action of theoretical quantities of ammonium hydrogen citrates. Tricalcium phosphate is dissolved by triammonium citrate, diammonium citrate, or monoammonium citrate. A large excess of triammonium citrate

however, is required, triammonium phosphate and calcium tetrammonium dicitrate being formed. By the action of diammonium citrate and monoammonium citrate, ammonium hydrogen phosphate and calcium ammonium hydrogen dicitrate, and monocalcium phosphate and calcium ammonium hydrogen dicitrate are formed respectively. Tricalcium phosphate is not readily attacked by citrates, and is dissolved only by a large excess of acid citrates. Since it is dissolved, however, to a considerable extent by triammonium citrate, it cannot be separated from dicalcium phosphate by means of this reagent. Tetracalcium phosphate is rapidly and completely dissolved by diammonium citrate, ammonium hydrogen phosphate and calcium ammonium hydrogen citrate being formed. It is also completely dissolved by monoammonium citrate, but less rapidly; monocalcium phosphate and calcium ammonium hydrogen dicitrate are found in this case. Diammonium citrate has a much greater solvent power than citric acid and might probably be advantageously used instead of citric acid for the evaluation of Thomas slags. Whilst dicalcium and tetracalcium phosphates are comparatively easily dissolved by acids such as carbonic acid and plant acids, and even by normal salts, such as triammonium citrate, tricalcium phosphate is much less readily attacked. Tricalcium phosphate may be converted into an easily assimilated form by the action of lime at a higher temperature. E. W. W.

Platinum Crucible for Carbon Combustions. JOHN V. R. STEHMAN (*J. Amer. Chem. Soc.*, 1903, 25, 237—242).—A modification of Shimer's process (*Abstr.*, 1899, ii, 694), in which the carbon derived from steel is burnt in a platinum crucible while a current of air is transmitted, the source of heat being a Bunsen burner or a blast lamp. For details of working and the cooling arrangement, the original article and illustration should be consulted. The chief improvement is the substitution of asbestos for the rubber washer. L. DE K.

Estimation of Small Quantities of Carbon Monoxide in Air. SPITTA (*Arch. Hygiene*, 1903, 46, [iii], 284—310).—The apparatus employed consists of a large glass vessel, holding from 10 to 11 litres, the capacity of which is exactly known. Its neck is closed by a glass stopper, through which pass two glass tubes provided with taps, one ending just inside the stopper, and the other, reaching to the bottom of the vessel, being bent so that its end is at the angle between the side and bottom. Two copper wires are also passed airtight through openings in the stopper, the longer one ending in a platinum cone which supports the lower pole of the oxidising apparatus, whilst the shorter copper wire is fastened to the upper part of the latter. The oxidising apparatus is composed of a silver coil, coated with black metallic palladium. This coil surrounds a glass tube containing a thermometer, partly surrounded by a nickel spiral, which is connected to the shorter copper wire. The vessel is filled with the air to be examined, as is also a second vessel of similar capacity, but containing only a thermometer and two tubes sealed through its stopper. The palladium coated coil is then heated to a temperature of 150—160° by passing an electric

current through the copper wires, 20 c.c. of pure hydrogen having been first passed into the vessel. The addition of hydrogen is necessary for the complete and expeditious combustion of the carbon monoxide. When the combustion is completed, the vessel is cooled by a stream of water, a measured quantity of standard barium hydroxide solution is added to each flask, and after absorption of the carbon dioxide has taken place the excess is titrated back with oxalic acid solution in each case. The difference between the amounts of carbon dioxide found in the two vessels is due to the conversion of carbon monoxide into dioxide.

W. P. S.

Gasometric Estimation of Carbon Dioxide by the Measurement of Liquid or Determination of Pressure. ALFRED WOHL (*Ber.*, 1903, 36, 1412—1417).—This is an application of principles already described (this vol., ii, 39); for details, the original should be consulted. Control analyses are given showing the degree of accuracy of the method.

W. A. D.

Suitability of Various Indicators for the Estimation of Alkali in Presence of Nitrite and Formate. M. WEGNER (*Zeit. anal. Chem.*, 1903, 42, 153—157).—For the estimation of the alkali in the product of the reduction of nitrates by formates in presence of alkali hydroxide (Goldschmidt's reaction), which takes place according to the equation $\text{NaNO}_3 + \text{CHO}_2\text{Na} + \text{NaHO} = \text{Na}_2\text{CO}_3 + \text{NaNO}_2 + \text{H}_2\text{O}$, the following indicators were tested: litmus, azolitmin, sodium alizarinsulphonate, gallein, methyl-orange, Wolff's salicylate indicator (*Abstr.*, 1900, ii, 435), resazurin, Congo red, *p*-nitrophenol, laemoid, rosolic acid, and iodeosin. Very good results were obtained with sodium alizarinsulphonate and gallein, but azolitmin, 'salicylate indicator,' and rosolic acid were also fairly satisfactory.

M. J. S.

Analysis of Sodium Nitrite. M. WEGNER (*Zeit. anal. Chem.*, 1903, 42, 157—159).—Whilst the permanganate method gives unexceptionable results with pure nitrites, it fails when formates are also present (see preceding abstract). In such cases, the nitrite can be titrated by means of *p*-sulphanilic acid. It is, however, necessary that the starch solution used as an indicator should be freshly prepared; even when one day old, its indications are untrustworthy.

M. J. S.

Separation and Estimation of Zinc by Electrolysis. AUGUSTE HOLLARD (*Bull. Soc. chim.*, 1903, [iii], 29, 266—269).—The well-known process of separating zinc by electrolysis from a solution containing potassium cyanide and a large excess of sodium hydroxide gives excellent results in the presence of aluminium. When iron is present, it is advisable to redissolve the ferruginous precipitate in a little sulphuric acid, and after neutralisation with sodium hydroxide to add this to the already electrolysed liquid, when the remainder of the zinc may be obtained. It is best to use a current of 0.1 ampere

and to deposit the metal on platinum gauze previously coated with copper. Zinc cannot be properly separated from nickel in this manner.

The method of depositing zinc electrolytically from its sulphate in the presence of organic salts and a slight excess of acetic acid does not work well in the presence of iron or aluminium. L. DE K.

Method of Separating Zinc from Nickel by Hydrogen Sulphide in a Solution containing Gallic Acid. ERNEST A. LEWIS (*Analyst*, 1903, 28, 93—97).—To a neutral or feebly acid solution of zinc and nickel containing not more than 0.6 gram of each metal (preferably as sulphate), 2 grams of gallic acid dissolved in hot water are added, and a current of hydrogen sulphide passed through the diluted and completely cooled solution. The zinc is precipitated as sulphide, and, after being collected on a filter, is washed, dried, and weighed as usual. The filtrate is evaporated to a bulk of 15 c.c., 30 c.c. of nitric acid are added, and heated until the solution turns green. It is then evaporated, after the addition of 1 c.c. of sulphuric acid, until the latter is volatilised, and any organic matter destroyed. The residue is dissolved in a little dilute sulphuric acid, filtered, the filtrate is diluted to 300 c.c. after adding 10 c.c. of concentrated ammonium hydroxide and 3 grams of ammonium oxalate, and the nickel deposited by electrolysis at a temperature of 40°. The method may be applied to the analysis of German silver and other alloys after removing the copper, tin, and lead in the usual manner. The nickel and zinc are then converted into sulphates before proceeding with the separation. W. P. S.

Quantitative Separations by Means of Persulphates in Acid Solution. III. MAX DITTRICH and C. HASSEL (*Ber.*, 1903, 36, 1423—1427. Compare this vol., ii, 107).—By the methods previously described, it is possible to separate manganese from cadmium, copper, and nickel, but not from mercury, silver, iron, or cobalt. T. M. L.

Analysis of Cobalt Compounds. H. COPAUX (*Bull. Soc. chim.*, 1903, [iii], 29, 301—306).—The heavy metals are precipitated by hydrogen sulphide, manganese, and zinc by sodium sulphide in presence of potassium cyanide, whilst iron is detected by ammonium thiocyanate. For the detection of nickel in cobalt compounds, the method of Piñerúa (*Abstr.*, 1897, ii, 387) is used in preference to those of Liebig and of Mond, Langer, and Quincke (*Trans.*, 1890, 57, 749), which are less delicate.

Cobalt is estimated in presence of nickel by precipitation as potassium cobaltic nitrite, $K_6Co_2(NO_2)_{12} \cdot 2H_2O$, solution of this precipitate in warm dilute sulphuric acid, and electrolysis after the addition of ammonium oxalate and excess of ammonium carbonate. The trustworthiness of this process is illustrated by a series of examples and by the analysis of an asbolan from New Caledonia. T. A. H.

Separation and Estimation of Antimony by Electrolysis. AUGUSTE HOLLARD (*Bull. Soc. chim.*, 1903, [iii], 29, 262—265).—Classen's sodium sulphide process is interfered with by the presence of copper (which is not quite insoluble in concentrated solutions of sodium hydrogen sulphide) and gives rise to the formation of polysulphides, which attack the deposited antimony. The modification suggested consists in adding to 200 c.c. of the sodium hydrogen sulphide solution of sp. gr. 1.22, 40 c.c. of a 20 per cent. solution of potassium cyanide. The cathode is composed of platinum gauze, and the strength of the current should be 0.1 ampere. Operating in this manner, the presence of small quantities of tin and arsenic acid is also without any ill-effect.

L. DE K.

The Colon Bacillus in Ground Waters. ELMER G. HORTON (*J. Hygiene*, 1903, 3, 155—158).—The fact that water is derived from a drilled well should not be taken as an absolute guarantee that it is potable. *Bacillus coli*, often found in such water, indicates pollution, and its presence condemns the water for drinking purposes.

W. D. H.

Microchemical Detection and Discrimination of the Phenols. T. HEINRICH BEHRENS (*Zeit. anal. Chem.*, 1903, 42, 141—152).—For the separation of the monohydric from the polyhydric phenols, advantage is taken of their relative solubility in benzene and water. The substance is dissolved in three times its volume of benzene (carbon tetrachloride if catechol is present), and the solution is shaken with double its volume of water. Polyhydric phenols pass into the water, the monohydric, together with the phenyl ethers (anisole, phenetole, guaiacol, eugenol), remain in the benzene.

Polyhydric Phenols.—The aqueous solution, after warming to expel benzene, is treated with lead acetate, which precipitates pyrogallol and catechol. The precipitate is decomposed with sulphuric acid, the excess of acid neutralised by calcium carbonate, the mass dried and treated with benzene to dissolve the catechol, and then with alcohol to extract pyrogallol. The filtrate from the lead precipitate is freed from lead by hydrogen sulphide and evaporated. From the residue, resorcinol is extracted by benzene, quinol and phloroglucinol by alcohol. After evaporating the alcohol and dissolving the residue in water, the addition of quinone precipitates the quinol as quinhydrone. If no precipitate is obtained, the solution may be distilled with dilute sulphuric acid and manganese dioxide, and quinone be looked for in the first drops of the distillate. The benzene extract is examined for resorcinol and orcinol by bromination.

Monohydric Phenols.—The original benzene solution is gently warmed to remove the solvent, and is then mixed with ten volumes of water and fractionally distilled. There pass over in succession anisole, phenetole, phenol, the three cresols, with guaiacol, xylenols, ψ -cumerol, thymol, eugenol, and the naphthols. The earlier fraction, if turbid, is gently shaken with a little benzene, which will dissolve anisole and phenetole with but little phenol. The ethers may then be recognised by nitrating. The fraction containing the cresols is mixed with alcohol and warmed with lime, which precipitates guaiacol ;

this is recognised by the red colour of its oily bromine derivative and by its characteristic calcium compound. Phenol yields crystalline tribromophenol, or may be identified by conversion into potassium picrate. The cresols also yield characteristic potassium salts of their nitro-derivatives. The fraction containing the xlenols is also treated with lime, which precipitates the eugenol. Thymol is examined for by shaking the distillate with benzene and oxidising with chromic acid to thymoquinone, which is then precipitated as its quinhedrone by adding quinol. If the later fractions exhibit crystalline flakes, the xylols and ψ -cumenol are to be looked for. Excess of sodium hydroxide is added, the solution is concentrated, treated with ammonium carbonate, and inoculated with traces of the respective phenols, the resulting crystals being recognised by their microscopical appearance. The naphthols yield characteristic compounds with picric acid.

The microscopic characters of the various precipitates are described.

M. J. S.

Estimation of Glycerol. A. BUISINE (*Compt. rend.*, 1903, 136, 1082—1083).—See this vol., i, 455.

Estimation of Glycerol in Crude Glycerols. JULIUS LEWKOWITSCH (*Analyst*, 1903, 28, 104—109).—Analyses are given showing that of recent years the dichromate method for estimating glycerol has tended to give results higher by several per cent. than those obtained by the acetin method. This is probably due to impurities in the crude glycerol which were not formerly present. Owing to the increase in price of raw materials, the cheapest fats and greases are worked up, yielding correspondingly impure glycerols. These impurities count as glycerol in the dichromate process.

W. P. S.

Pentose Estimations. ERNST UNGER and RICHARD JÄGER (*Ber.*, 1903, 36, 1222—1229. Compare this vol., ii, 187).—In order to obtain good results for the estimation of furfuraldehyde by the barbituric acid method, it is essential that the acid employed shall be completely soluble in 12 per cent. hydrochloric acid and that at least 6 times the calculated amount of the acid be employed. If the volume of the liquid is more than 500 c.c., then 8 times the calculated quantity should be introduced. As a small amount of the condensation product remains in solution, it is advisable to add to the weight of the precipitate 1.22 mg. for each 100 c.c. of original solution. The results obtained for pure arabinose and xylose are practically the same whether this method or the phloroglucinol method is employed.

When sucrose, starch, and cellulose are boiled with 12 per cent. hydrochloric acid or the distillate treated with barbituric acid, no precipitates are obtained, although small amounts of precipitates are obtained when phloroglucinol is employed. When, however, a mixture of starch and xylose is distilled in the same manner, the amount of precipitate is in excess of that required for the xylose alone, and the precipitate has a characteristic yellowish-green colour. This excess is avoided if the material is previously extracted with water or 1 per

cent. hydrochloric acid. The latter method can be more readily carried out, and when the heating is continued for only 10 minutes good results may be obtained.
J. J. S.

General Reaction of Aldehydes. E. RIEGLER (*Zeit. anal. Chem.*, 1903, 42, 168—170).—The reaction described by the author for formaldehyde and lactose (*Abstr.*, 1901, ii, 206) is a general one for substances of aldehydic character. It may be simplified by using phenylhydrazine oxalate instead of the hydrochloride with sodium acetate. To 5 c.c. of the aldehyde solution (which must be of not more than 1 per cent. strength) there are added 5 c.c. of water and a few crystals of phenylhydrazine oxalate. After warming until this is dissolved, 10 c.c. of 10 per cent. potassium hydroxide solution are added, the test-tube is closed with a caoutchouc stopper and vigorously shaken. If an aldehyde or sugar of aldehydic constitution is present, a rose-red colour is developed in a few seconds; the appearance of a similar colour later will occur in the absence of aldehydes. The test may be applied directly to diabetic urine, brandy, &c.
M. J. S.

Estimation of Vanillin in Vanilla. A. MOULIN (*Bull. Soc. chim.*, 1903, [iii], 29, 278—280).—The process is based on the conversion of vanillin into the yellow methyl picrate.

The standard solution is prepared by dissolving 0.5 gram of vanillin in 20 c.c. of a mixture of 10 c.c. of sulphuric and 100 c.c. of (?glacial) acetic acid; a few crystals of potassium nitrate are added, and the mixture is heated in a water-bath at 60° for an hour. After remaining for another 12 hours, the solution is diluted to 100 c.c., and a series of comparison liquids is made by successively diluting 2, 4, 6 c.c. to 100 c.c.

The solution obtained by extracting 3—6 grams of the commercial sample with ether is decolorised with 10 grams of animal charcoal, and filtered through cotton-wool. After evaporating the ether, the residue is treated with the acid mixture and potassium nitrate as directed. After diluting with water and filtering from any resinous matter, the filtrate is made up to 100 c.c. and compared with the coloured standard solutions.
L. DE K.

Polarimetric Estimation of Tartaric Acid and Tartrates. FRED. W. RICHARDSON and J. C. GREGORY (*J. Soc. Chem. Ind.*, 1903, 21, 405—409).—Advantage is taken of the fact that alkalis increase the optical activity of tartaric acid threefold, whilst ammonium molybdate increases it some sixtyfold. 0.625 gram of tartaric acid is placed in a flask, together with three times as much ammonium molybdate. After diluting with water to 25 c.c., a reading is taken in a 100 mm. tube at 15.5°, the light being passed through a very reddish-orange screen. Tables are given for calculating the amount of tartaric acid present. Pure tartaric acid under the above conditions gives $[\alpha]_D +790^\circ$. Details are also given of the process as applied to the analysis of normal tartrates, seidlitz powders, &c. (compare *Abstr.*, 1903, ii, 112).
W. P. S.

Iodine Absorption of Oils and Fats. L. M. TOLMAN and L. S. MUNSON (*J. Amer. Chem. Soc.*, 1903, 25, 244—251).—A comparison of methods for the estimation of the iodine number of fats. Owing to certain inconveniences attaching to the original Hübl (iodine-mercuric chloride) method, a proposal has been made by Hanūs to use a solution of iodine monobromide in glacial acetic acid, and Wijs has proposed a solution of iodine monochloride in the same solvent. From the authors' researches, it seems that the Hanūs method (Abstr., 1902, ii, 112) is somewhat preferable to Wijs's process (Abstr., 1898, ii, 412, 491, 466), as the reagent is more readily prepared. L. DE K.

Detection of Heated Milk by means of the Guaiacum Test. JULIUS ZINK (*Milch. Zeit.*, 1903, 32, 193—195, 211—215).—The addition of a drop of a very dilute solution of hydrogen peroxide causes freshly prepared or otherwise inactive guaiacum tincture to give a blue coloration with raw milk. With a tincture which already gives the coloration, the addition of hydrogen peroxide causes the production of a more intense and stable colour. Boiled milk, even after some hours, gives no coloration. It was found preferable to apply the test as a "zone reaction" (compare Abstr., 1902, ii, 539).

W. P. S.

Estimation of Fat in Milk. M. SIEGFELD (*Zeit. Nahr. Genussm.*, 1903, 6, 259—271).—Numerous estimations of fat in milk are given, the analyses being made for the purpose of comparing the processes of Adams, Gerber, and Gottlieb with one another. The results of all three methods closely agreed. Experiments were also undertaken to ascertain the influence of water and acetic anhydride in the ether used for the extractions on the results, and also the errors due to drying the extracted fats at temperatures above 100°; to ether-soluble substances in the paper strips; to the action of sulphuric acid on amyl alcohol, &c. Within moderate limits, the results were not affected.

W. P. S.

Estimation of Fat in Animal Matters. W. GLIKIN (*Pflüger's Archiv*, 1903, 95, 107—145).—The first part of this paper is historical and critical. The second deals with an examination of methods generally employed, together with details of a new process. Rosenfeld's method gave the highest results, but the fat was contaminated with nitrogenous substances (lecithin). The lowest results were yielded by Voit's method, with a correspondingly larger quantity of impurity. The author purifies the fatty residues obtained by either dissolving them directly in acetone and filtering off the insoluble lecithin, or dissolving in a little chloroform and then precipitating with acetone.

W. P. S.

Detection of Morphine. C. REICHARD (*Zeit. anal. Chem.*, 1903, 42, 95—100).—Any morphine compound added in the solid state to a saturated solution of titanous oxide in concentrated sulphuric acid produces a reddish-brown or black colour of great intensity. On adding a little water, the mixture becomes colourless. A morphine solution may be used, but it must be added in such a way as not to

mix with the sulphuric acid; the colour is then produced at the zone of contact. Morphine gives also characteristic reactions with vanadic and tungstic acids. A concentrated solution of ammonium metavanadate, to which sufficient sulphuric acid has been added to redissolve the yellow vanadic acid at first precipitated, gives a persistent green or bluish-green coloration when warmed with a morphine salt. An acidified solution of sodium tungstate (not stronger than 0.1 per cent.) gives a transient blue or violet coloration with morphine. Morphine also reduces chromic acid. M. J. S.

Estimation of Morphine by means of its Reducing Action on Silver Nitrate. GEORG HEYL (*Chem. Centr.*, 1903, i, 480; from *Pharm. Zeit.*, 48, 36—38).—Reichard's process (*Abstr.*, 1901, ii, 140) is useless for the determination of morphine in opium, &c., as the reaction between morphine and silver nitrate is not a quantitative one (compare also Schidrowitz, *Abstr.*, 1902, ii, 483). L. DE K.

Estimation of Theobromine in Cocoa. J. DECKER (*Rev. Intern. Falsif.*, 1903, 16, 12—13).—In *Cocoa Nibs*.—Fifty grams of the powdered sample are mixed with 25 grams of magnesium hydroxide and 500 c.c. of water and boiled for an hour. The filtrate and washings are evaporated to dryness and the residue extracted several times with boiling alcohol of 95 per cent. by volume. On evaporating the solution to a small bulk, the theobromine will crystallise and may be collected and weighed, but a small quantity remains in solution. It is, therefore, better to substitute chloroform for alcohol and then to evaporate to dryness, when pure, colourless theobromine is obtained.

In Chocolate and Prepared Cocoas.—Ten grams of the material are boiled with 5 grams of calcined magnesia and 300 c.c. of water and boiled for an hour in a reflux apparatus, the hot liquid is filtered and the residue is well pressed, and then again boiled for a quarter of an hour with 150 c.c. of water. The united filtrates are evaporated to dryness on the water-bath with addition of sand, and the powdered residue extracted three times in succession with 100 c.c. of boiling chloroform. The chloroform is recovered by distillation and the residue dried for half an hour at 100° and weighed. It may be freed from any caffeine by treatment with cold benzene, in which that alkaloid is readily soluble. L. DE K.

Identity Test for Condurang Extract. RICHARD FIRBAS (*Chem. Centr.*, 1903, i, 538—539; from *Zeit. Österr. Apoth. Ver.*, 1903, 41, 57—60).—The fluid extract is slightly evaporated to expel any alcohol, the residue when cold is mixed with sodium chloride solution, and the precipitated condurangin collected on a filter and washed with brine. The precipitate is then dissolved in chloroform, the almost colourless solution shaken with a mixture of equal parts of sulphuric or hydrochloric acid and alcohol, and gently heated, when a green coloration will appear which turns a fine bluish-green on adding a trace of ferric chloride. This reaction is a test for digitalin proposed by Lafon, but it is much better suited for condurangin. L. DE K.

Volumetric Estimation of True Casein and other Proteids in Milk. GEORGES DENIGÈS (*Rev. Intern. Falsif.*, 1903, 16, 18—19).—*Total Proteids.*—Into a 200 c.c. flask are introduced 25 c.c. of milk, 1 c.c. of a 30 per cent. solution of potassium oxalate, and, after shaking, 20 c.c. of mercury solution (13.55 grams of mercuric chloride, 36 grams of potassium iodide and water to 1 litre). After introducing 2 c.c. of glacial acetic acid and diluting to 200 c.c., the liquid is filtered and 100 c.c. of the filtrate are poured into a flask into which have been already put 10 c.c. of solution of potassium cyanide equivalent to decinormal silver and 15 c.c. of ammonia. The mixture is now titrated with *N*/10 silver nitrate until a faint but persistent turbidity is formed. From the result, the amount of proteid is calculated by aid of a table given in the original.

Proteids not Coagulable by Acetic Acid.—Fifty c.c. of milk are mixed with 180 c.c. of water and 2 c.c. of glacial acetic acid, then diluted to 250 c.c. and filtered. One hundred and twenty-five c.c. of the filtrate representing 25 c.c. of milk are then treated as before. The difference between the results represents the true casein. L. DE K.

Van Deen's Reaction. N. TARUGI (*Gazzetta*, 1902, 32, ii, 505—511).—The fact that hæmoglobin yields a blue colour when mixed with old turpentine oil and alcoholic tincture of guaiacum resin has been explained by supposing that the hæmoglobin acts as a carrier of ozone from the turpentine oil to the guaiacum resin. Recent investigations have, however, shown the existence of a series of hyperacids which, under certain conditions, yield a blue coloration with guaiacum resin, and in many cases to which van Deen's reaction is applied, the conditions obtaining are such as admit of the production of these acids. In some instances, also, the blue colour is produced with substances which are not oxidising agents. Thus, on mixing a drop of potassium thiocyanate solution with recently prepared alcoholic tincture of guaiacum, the liquid remains quite colourless, but the addition of old turpentine oil produces an intense blue coloration. The author shows that this depends on the oxidation of the sulphur present to Caro's acid. When hydrogen peroxide acts on concentrated potassium thiocyanate solution acidified with sulphuric acid, it yields first Caro's acid and ultimately pseudothiocyanogen, according to the equations: (1) $\text{HSCN} + 4\text{H}_2\text{O}_2 + \text{H}_2\text{O} = \text{HCN} + 4\text{H}_2\text{O} + \text{H}_2\text{SO}_5$; (2) $\text{H}_2\text{SO}_5 + \text{HCN} = \text{H}_2\text{SO}_4 + \text{HCN}\text{O}$; (3) $2\text{HSCN} + \text{HCN}\text{O} = \text{H}_2\text{O} + \text{C}_3\text{HN}_3\text{S}_2$. Pseudothiocyanogen acts similarly to hydrogen peroxide.

The authors conclude that the production of van Deen's reaction by hæmoglobin depends on the formation of Caro's acid by the oxidation of the sulphur of the hæmoglobin, and that the latter contains the thiocyanogen group. T. H. P.

Reaction of Cystin. ALI RIZA (*Bull. Soc. chim.*, 1903, [iii], 249—250).—Mercuric sulphate added to solutions of cystin precipitates a white, amorphous compound, from which, by treatment with hydrogen sulphide, pure cystin can be regenerated. This reaction distinguishes cystin from other urinary deposits. Mercuric chloride, nitrate, and acetate furnish no insoluble compounds with cystin, but do so with cysteine. T. A. H.

General and Physical Chemistry.

Influence Exerted by the Introduction of Double Linkings into the Nuclei containing the Asymmetric Carbon Atom on the Rotatory Power of Cyclic Molecules. ALBIN HALLER (*Compt. rend.*, 1903, 136, 1222—1226).—See this vol., i, 563.

New Series of Lines in the Spectrum of Magnesium. A. FOWLER (*Proc. Roy. Soc.*, 1903, 71, 419—420).—With an arc discharge between magnesium rods, four lines, not hitherto noticed, appear in the spectrum, the wave-lengths (in air) being 4511·4, 4251·0, 4106·8, and 4018·3. The author considers that these lines constitute a regular series, associated with the much stronger series described by Rydberg. This view is confirmed by calculation, and it is concluded that the arc spectrum of magnesium includes two subordinate series of single lines in addition to the two well-known subordinate series of triplets, J. C. P.

Emanations of Radium. Sir WILLIAM CROOKES (*Proc. Roy. Soc.*, 1903, 71, 405—408).—In presence of some feebly luminous radium nitrate, a barium platinocyanide screen glowed with a green light, the phosphorescence disappearing whenever the screen was removed. A zinc sulphide or blende screen was found to be almost as luminous as the platinocyanide screen under the same conditions, but the residual phosphorescence lasted for some time. When the blende screen is tapped with a knife-point, a sudden spark of light is produced, and a scratch gives rise to an evanescent luminous line. An accidental contact of a few tiny particles of the radium salt with the blende screen caused the surface to become dotted over with specks of green light markedly larger than the inducing particles. A microscope, in a dark room, shows each spot to have a dull centre with a surrounding luminous halo, whilst outside the halo the dark surface of the screen scintillates with sparks of light. When solid radium nitrate is brought near the screen, the scintillations increase rapidly in number and intensity with the effect that after a certain point there is a residual phosphorescent glow, not observed when the scintillating points are few. A platinum wire, dipped in radium nitrate solution and dried, has the same effect if brought near the screen; if allowed to touch the screen, it produces a luminous spot, which is an active centre of scintillations for weeks afterwards. No variation in the scintillations could be detected when air was blown between the radium salt and the screen. Polonium sub-nitrate has a similar effect on a zinc sulphide screen, but the scintillations are less numerous.

Comparison of the effects produced on platinocyanide and zinc sulphide screens by exposure to radium nitrate and polonium sub-

nitrate leads to the view that the luminosity on the blende screen, whether due to radium or polonium, is caused by emanations which will not penetrate card. The scintillations caused by these emanations are distinct on the blende and feeble on the platinocyanide screen, because with the latter the sparks are seen on a luminous ground of general phosphorescence.

The scintillations described above are regarded as associated with the impacts on the screen of the electrons thrown off by the radium salt, and from his experiments the author concludes that the number of electrons hitting the screen in a given time is not inconceivably great.

J. C. P.

Emanation of Radium and its Coefficient of Diffusion into Air. PIERRE CURIE and J. DAUNE (*Compt. rend.*, 1903, 136, 1314—1316. Compare Abstr., 1901, ii, 216; 1902, ii, 50).—The rate of change in intensity of radiation emitted by the walls of a closed vessel containing radium takes place according to the law $dI/dt = -bI$, where b has the value 2.01×10^{-6} seconds. When the radium is contained in a glass vessel communicating with the air by a capillary tube, the rate of change follows the same law, but b has a higher value than in the former case, due to diffusion of the radium emanation into the air. The difference (a) in the two values of b is equal to Ks/lv , where K is the coefficient of diffusion, s and l the sectional area of the bore of the capillary tube and the length of the latter respectively, and v is the volume of the reservoir. K , at 10° and under the ordinary pressure, has the value 0.1 C.G.S. units (the corresponding values for carbon dioxide and ether being respectively 0.15 and 0.09). A table of experimental results establishing the validity of this relation is given in the original. This result indicates that the emanation of radium behaves like a gas (compare Rutherford and Brooks, Abstr., 1902, ii, 438). Further evidence of this was obtained by showing that a given quantity of radium emanation, as measured by intensity of radiation, divides itself between two vessels, in inter-communication but otherwise closed, in proportion to their respective volumes, so long as the temperatures of both vessels are the same, but that when the temperature of one vessel is below that of the second, there is an increase in intensity of radiation in the colder vessel proportional to the lowering of temperature. It is possible, by enclosing radium in a vessel closed by a sealed capillary tube, to concentrate the emanation in the latter by placing it in liquid air and melting off the capillary tube.

T. A. H.

Condensation of the Radioactive Emanations. ERNEST RUTHERFORD and FREDERICK SODDY (*Phil. Mag.*, 1903, [vi], 5, 561—576).—It is shown that the thorium emanation begins to condense when cooled to about -120° , and none can be detected after passage through a tube cooled to -155° . Radium emanations also condense if cooled to about -154° , and begin to volatilise at about the same temperature, the point when volatilisation is first detected being well marked and distinct, namely, in a stationary atmosphere, at -150° , and

in a steady stream, at -153° . With a gradually rising temperature, the whole of the emanation volatilises within a few degrees, and the rate of volatilisation increases very rapidly at about a degree above the temperature when it is first observable. The emanation hence appears to possess a distinct vapour pressure, and it is indicated that the emanation actually consists of matter in the gaseous state.

L. M. J.

Radioactive Change. ERNEST RUTHERFORD and FREDERICK SODDY (*Phil. Mag.*, 1903, [vi], 5, 576—591).—The radioactivity of radium, thorium, and uranium is associated with chemical change resulting in the production of new kinds of matter, thus, thorium produces thorium α , &c. It has been shown that the X-rays are material, and the mass of the projected particle is of the same order of magnitude as the hydrogen atom; these rays, moreover, represent over 99 per cent. of the energy radiated, and the author considers that this expulsion of matter is not merely an accompaniment of the change, but that it is the change itself. The decrease of activity of a radioactive substance has been proved to be of the form $I_t/I_0 = e^{\lambda t}$, where I is the ionisation current due to the radiation. This leads to the result that the rate of change of the system is proportional to the amount remaining unchanged. This law is that of a unimolecular chemical change, and as the radioactivity is a specific property of the element, the changing system must be the chemical atom; the change is hence the disintegration of the atom. The authors apply the term "metabolon" to the resulting unstable atoms which undergo further change. The total energy of radiation of 1 gram of radium is probably between 10^8 and 10^{10} gram calories, and is hence many thousand times greater than any known chemical change, and the rate of dissipation of this energy leads the authors to the belief that the life of radium cannot be more than a few thousand years.

L. M. J.

The Rays Emitted by Radioactive Lead. A. KORN and EDUARD STRAUSS (*Compt. rend.*, 1903, 136, 1312—1313. Compare Abstr., 1901, ii, 19, 159, 216, 385, and 655).—The photo-chemical effect produced by radioactive lead sulphate is increased by previous exposure to cathode rays, but the electric effect remains uninfluenced by this treatment. It is suggested that the radiation emitted by radioactive lead is of two kinds, namely, a radiation capable of acting on sensitised plates, to which aluminium, glass, and other substances are transparent, and which is slightly electrically active as the result of the ionisation of the air, and a second form (probably an emanation of infinitely small particles) having less penetrative power, to which the electric effects are mainly due. The effects produced by the former are enhanced by previous exposure of the radioactive material to cathode rays, whilst an increase in electrical effect is only brought about by this means in the case of preparations the activity of which has been impaired by chemical treatment.

T. A. H.

Oxidation and Reduction Potentials. KARL SCHÄUM and RICHARD VON DER LINDE (*Zeit. Elektrochem.*, 1903, 9, 406—409).—The potentials of a platinum electrode in solutions containing mixtures of potassium ferricyanide and sodium ferrocyanide at 25° and 50° are measured (see Abstr., 1900, ii, 2). From van't Hoff's equation, $\pi = RT/F \log k C_i / C_o$, values of k are calculated and found to be sufficiently constant when the molecular concentrations of the ferri- and ferro-cyanides, C_i and C_o , are used. The heat of the reaction $\text{FeCy}_6''' \rightarrow \text{FeCy}_6''''$ is also calculated by means of Helmholtz's equation and by van't Hoff's formula $\log K/K' = q/R(1/T - 1/T')$, the first giving 21730 cal. and the second 21670 cal. per molecule.

Further experiments were also made on mixtures of a sulphite and a sulphate, but no satisfactory results were obtained. It was found that the effect of benzyl alcohol previously observed (Abstr., 1901, ii, 300) was due to an experimental error, and the results given in the paper mentioned are withdrawn. T. E.

Law Relating to the Electromotive Forces Developed by Reciprocal Actions of Saline Solutions. MARCELLIN BERTHELOT (*Compt. rend.*, 1903, 136, 1109—1118).—The law already established by the author (this vol., ii, 258, 259) that the *E.M.F.* developed by the neutralisation of a base by an acid is equal to the sum of those developed by the action (*a*) of the acid, and (*b*) of the base on the corresponding salt has been confirmed by experiments in which the metals mercury, copper, zinc, lead, and silver have been employed as electrodes in place of platinum. The law therefore holds good for polarising electrodes.

The measurements already made show that the *E.M.F.* developed by the action of acids on bases are similar for similarly constituted substances, and are in close agreement with those calculated from the heats of neutralisation. This relationship is, however, only true for those cases in which this heat is the principal source of electric energy, and is not valid for the *E.M.F.* developed by the action of acids or bases on the corresponding salts.

The electric differences established in the latter cases are, like those developed during the solution of gases and the diffusion of liquids, obtained at the expense of the neighbouring medium, and are not due to exothermic reactions. The differences shown in external work in cells of these two orders is to be attributed to the different sources from which the energy is drawn. T. A. H.

Electrical Conductivity of Solutions in Amylamine. LOUIS KAHLENBERG and OTTO E. RUHOFF (*J. Physical Chem.*, 1903, 7, 254—258).—The dielectric constant of amylamine (4.5) is slightly greater than that of chloroform (3.9), and hence it would be expected that solutions in this solvent would be found to be electrolytes. Silver nitrate, cadmium iodide, and ferric chloride are soluble in amylamine, and all were found to yield conducting solutions. In the case of the silver nitrate and cadmium iodide solutions, the molecular conductivity passes through a maximum, being exceedingly low for the more dilute solutions. Such cases, which are found also in the case of aqueous solutions, do not admit of explanation by the theory of Arrhenius.

Both solutions become very viscous near the saturation point, and by cooling the cadmium iodide solution needle-shaped crystals are obtained which the authors consider to be an additive product of solute and solvent.

L. M. J.

Residual Conductivity and Ionisation of Solid Paraffin under the Influence of Radium Radiation. HENRI BECQUEREL (*Compt. rend.*, 1903, 136, 1173—1176).—When solid paraffin is exposed to the radiation from radium, it acquires a decided conductivity. This was proved by placing a copper cylinder in a glass tube, then supporting a smaller aluminium cylinder concentrically within this. The annular space was filled with paraffin. The copper was connected with a source of electricity and the aluminium with an electrometer. Under ordinary conditions, the electrometer indicated no charge, but when a tube of radium chloride was lowered into the aluminium cylinder the electrometer showed that a current was passing through the paraffin. When the radium salt was removed, the current gradually diminished. That the effect was not due to the molecular instability of the solidified paraffin was proved by experimenting with paraffin the day after it had solidified, and again after it had been kept solid for thirteen months.

The analogy of this phenomenon with that which is observed when X-rays pass through dielectrics leads to the view that the radium radiation produces effects of the same kind in all dielectrics—solid, liquid, and gaseous.

J. McC.

Determination of Constitution by Qualitative Migration Experiments. ROBERT KREMAN (Zeit. anorg. Chem., 1903, 35, 48—54. Compare this vol., ii, 54).—A reply to Bredig (this vol., ii, 263). The author does not admit that there is practically any difference between his views on the constitution of methyl-orange and those of Winkelblech (Abstr., 1901, ii, 370). Bredig has not clearly stated his view, and it is not clear whether he regards actual formation of cations and anions as a criterion of an amphoteric electrolyte and if he regards methyl-orange as such.

Contrary to Bredig's opinion, the author regards a qualitative determination of the direction of migration as eminently sufficient to characterise an ion as a cation or an anion.

Incidentally, it is mentioned that Calvert (Abstr., 1902, ii, 10) in his migration experiments in agar-agar has not considered the possible influence of cataphoresis.

The order of magnitude of the migration of zinc and chromium in alkaline solution is sufficient to show that it is not migration in a colloidal solution which is taking place as suggested by Bredig.

J. McC.

Determination of the Thermal Conductivity of Argon and Helium by Schleiermacher's Method. WALTHER SCHWARZE (*Ann. Physik.*, 1903, [iv], 11, 303—330).—According to the kinetic gas theory, $k = f \cdot \eta \cdot c_v$, where k , η , and c_v are the thermal conductivity, the viscosity, and the specific heat respectively, whilst f is a constant. The author has found for argon $k = 0.00003894$, and for helium $k = 0.0003386$, the accuracy of the method being guaranteed by the value

0.0000569 found for air, in close agreement with previous observers. Conran and Neugebauer have arrived theoretically at the value 1.6027 for f , but when the author's experimental results are used in the above equation, $f=2.501$ for argon, and $f=2.507$ for helium. The value 2.50 for the constant f is in harmony with Boltzmann's development of Maxwell's theory.

J. C. P.

Thermal Conductivity of Crystallised Bismuth. F. LOUIS PERROT (*Compt. rend.*, 1903, 136, 1246—1248).—The thermal conductivity of bismuth is greatest in the direction of cleavage. The mean of the square of the ratio of the thermal conductivities perpendicular to, and parallel to, the axis of the crystal is 1.342. There appears to be a connection between the conductivities and the ratio of the thermoelectric forces (*Arch. Sci. phys. nat. Genève*, 1898, 6, 105, 229; *ibid.*, 1899, 7, 149) of various specimens of the metal.

J. McC.

Simple Relation between the Molecular Heat of Solidification and the Boiling Point. III. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1903, [vii], 28, 5—58. Compare this vol., ii, 267, 353).—The author summarises some results which have already been published and gives certain consequences which can be deduced from the relationship $(L+S)/T=30$, already established by him. The equation may be put into a form analogous to the equation of condition for gases, and from this it is deduced that the quantity of heat developed when 1 gram of any gas passes into the solid state can be calculated by dividing its absolute boiling point by its theoretical density and multiplying by 1.039.

It is shown how deviations from the relationship $(L+S)/T=30$ may be satisfactorily accounted for by polymerisation and how the results may be used for determining the degree of molecular association. Although in most cases the sum of L and S is determined, it is possible to ascertain their separate values. Since $L+S=M(l+s)$, where M is the molecular weight, the determination of the specific heat of solidification and the boiling point may be used to calculate the molecular weight; the results obtained in this way agree well for sulphur, acetic acid, and some other substances with those found by other methods. It is noticeable that for mercury the molecular weight at 357° corresponds with the formula $\text{Hg}_{1.1}$.

Amongst other consequences deduced from the relationship, it may be pointed out that the author is able to calculate the heat of formation of some compounds from the gaseous constituents, and these are very different from the heats of formation ordinarily accepted. In this connection, the stability of compounds with respect to dissociation is discussed.

The results obtained are used for determining the composition of the hydrates of several gases.

In conclusion, the author states the following as a general law:—In all reversible phenomena, physical or chemical, when a molecule of any gas passes into the solid state, the heat developed is proportional to the absolute boiling point of the substance.

J. McC.

Landsberger's Method for Determining Molecular Weights. RICHARD MEYER and PAUL JAEGER (*Ber.*, 1903, 36, 1555—1560. Compare Lehner, this vol., ii, 411).—Landsberger's apparatus is slightly modified so as to be available for solvents which are hygroscopic and of higher boiling point, such, for instance, as acetic acid. The special features are as follows: the vapour mantle surrounding the boiling vessel contains a quantity of the solvent which is kept boiling throughout an experiment so that condensation in the boiling-vessel is, as far as possible, avoided. The cold air in the vapour generator is expelled by a preliminary heating and is not passed into the boiling vessel, which would otherwise be cooled by it. Instead of determining the elevation in the boiling point of the pure solvent, a differential method is adopted by which the boiling points of two solutions of known concentration are observed. Finally, drying tubes are attached to prevent access of atmospheric moisture. For details, the original should be consulted, in which results are quoted showing the degree of accuracy of the method. W. A. D.

Depression of the Freezing Point by Non-electrolytes in Concentrated Aqueous Solutions. W. A. ROTH (*Zeit. physikal. Chem.*, 1903, 43, 539—564).—The causes of the deviations from van't Hoff's law exhibited by concentrated solutions are discussed, and on the basis of Jahn's theoretical work (*Abstr.*, 1902, ii, 597) an attempt is made to deduce quantitatively the result of a mutual interaction of the dissolved molecules. In two cases, namely, solutions of glycerol and sucrose, it is shown that there is parallelism between abnormal freezing point depression and the extent to which the presence of these solutes affects the solubility of gases.

Depressions of the freezing point in fairly concentrated solutions of dextrose, acetic acid, thiocarbamide, glycine, and chloral hydrate have been carefully determined, the apparatus employed resembling those used by Abegg (*Abstr.*, 1896, ii, 587) and Hausrath (this vol., ii, 61). Acetic acid (examined up to 6.5 per cent. concentration) and glycine (up to 6.3 per cent. concentration) both give too small depressions; in the former case, this is due to association; in the latter case, to association or mutual interaction of the solute molecules. In the cases of dextrose (examined as far as 16.6 per cent. concentration) and chloral hydrate (examined as far as 19.5 per cent. concentration), the depressions are too great; up to normal concentration, the results can be accounted for on the hypothesis of a mutual interaction, represented by a constant function; if Jahn's formula (*loc. cit.*) is to be adhered to for more concentrated solutions, the interaction must vary enormously with the temperature. It is more probable, however, that the formula does not hold beyond a certain point. In the case of thiocarbamide (up to 2.9 per cent. solution), the depressions are too small, but they cannot be quantitatively accounted for.

Freshly prepared concentrated solutions of dextrose give too small values of the depression, but these gradually increase to constant final values, the increase running parallel with the falling off in the birotation.

J. C. P.

Experimental Examination of the Thermodynamical Relation between the Heat of Solution and the Change of Solubility with Temperature in the Case of Dissociated Substances. ARTHUR A. NOYES and G. V. SAMMET (*Zeit. physikal. Chem.*, 1903, 43, 513—538).—According to van't Hoff, $L/RT^2 = i \cdot d(\log iS)/dT$, where S is the solubility, i the ionisation coefficient, and L the heat of solution of a dissociated substance. The heat of solution is here to be interpreted as the total heat effect accompanying the solution of 1 mol. of the substance in a quantity of water just sufficient to give a saturated solution. The difference of opinion that has arisen between Noyes and van Laar (compare Noyes, *Abstr.*, 1898, ii, 552; van Laar, *Abstr.*, 1899, ii, 11, 545; Noyes, *ibid.*, 401) in reference to the above formula is chiefly due to a different interpretation of the "heat of solution."

In order to bring the above equation to the test of experiment, the authors have determined (1) the heats of solution at 20°, (2) the solubilities at 10—30°, (3) the electrical conductivities at 10—30°, of *o*-nitrobenzoic acid and potassium perchlorate. With the aid of the second and third sets of experiments, the heats of solution have been calculated, and the values thus obtained have been compared with those directly determined. In the case of *o*-nitrobenzoic acid, the calculated value for L is 6480 cal., as compared with 6025 cal. actually found. Experimental errors are too small to account for this difference, and the authors suggest that *o*-nitrobenzoic acid may exist in solution partly as double molecules; association of this kind to the extent of 20 per cent. would fully explain the discrepancy. In the case of potassium perchlorate, the calculated value of the heat of solution is 12270 cal., whilst actual determination gives 12130 cal. Since the calculation involves the relation $\alpha = \Lambda/\Lambda_\infty$, this close agreement is regarded by the authors as evidence that the conductivity is a correct measure of the dissociation.

J. C. P.

Fermentations and Heat Change. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1903, 37, 383—395).—The heat changes of a number of processes of fermentation has been studied by the aid of the heats of combustion of the various substances, no account being taken of heats of solution or neutralisation.

Hydrolytic processes, for example, the hydrolysis of ethyl butyrate by lipase, maltose or α -methylglucoside by maltase, sucrose by invertase, lactose by lactase, and salicin or helicin by emulsin, are usually feebly exothermic, the heat change being but small. Such reactions in which a state of equilibrium exists should be but little affected by alterations in temperature.

The fermentation of urea; alcoholic fermentation; lactic and butyric fermentations; the oxidation of salicylaldehyde, and other processes of oxidation are reactions accompanied by a high positive heat change. If certain processes of reduction are to be regarded as of a fermentative nature, for example, the reduction of chloral hydrate and of butylchloral hydrate, they differ from other fermentative reactions as they are all of an endothermic nature.

J. J. S.

Supersaturated Solutions. GEORGE JAFFÉ (*Zeit. physikal. Chem.*, 1903, 43, 565—594).—According to Ostwald, supersaturated solutions may be either metastable or labile; in the first case, the solutions are permanent, in the second, they crystallise immediately. The question arises whether there is a sharp line of demarcation between the two classes, or whether crystallisation is simply a matter of time in the first case as in the second. In connection with this point, the author has carried out a large number of experiments, mainly with supersaturated solutions of potassium nitrate. In a first series, the life duration of a supersaturated solution was determined, the containing tube being immersed in a thermostat at 20°. At this temperature, under ordinary conditions, it is possible to dissolve 31.2 parts of nitrate in 100 parts of water, but it was found that solutions containing up to 58 parts of salt to 100 parts of water could be kept for many days in a sealed tube. Solutions containing more salt crystallised very rapidly, that is, within a minute or so. The limit, however, is by no means definite, and parallel experiments with the same solution may give quite different results. In general, it was shown that the metastable field could be very much enlarged by mechanically purifying the solutions. It appears that there are causes of crystallisation which act differently on solutions of different concentration, and sometimes initiate solidification only after a considerable lapse of time. These [nuclei are insoluble, and to effect their removal the solutions employed by the author were generally filtered 10—12 times.

In a second series of experiments, a supersaturated solution was slowly cooled, and the temperature was found at which spontaneous crystallisation set in. No general conclusions could be drawn, and for details the original must be consulted, where experiments with sodium and potassium chlorates, potassium and ammonium chlorides, potassium dichromate, and sodium sulphate are also described.

It was observed that when supersaturated solutions of potassium nitrate had been properly purified, the crystals produced by spontaneous crystallisation were of the unstable, rhombohedral form. Similarly, from supersaturated solutions of sodium sulphate, the heptahydrate is deposited by spontaneous crystallisation at the ordinary temperature. In the case of potassium nitrate, the slightest mechanical disturbance causes a further separation of the rhombic form. By analysis of solutions saturated with the rhombohedral form, the solubility of the latter has been determined. At the ordinary temperature, as might be expected, it is more soluble than the stable rhombic form.

J. C. P.

Colloidal Solution; the Globulin System. W. B. HARDY (*Proc. Physiol. Soc.*, 1903, xxvi—xxix; *J. Physiol.*, 29).—The globulin used was precipitated from diluted serum by acetic acid, and after purification dissolved in very weak acetic acid; the solution is introduced into a cell, and acetic acid of the same concentration is poured over its surface. If this is placed in an electric field, the opalescent proteid solution is seen to move with uniform velocity from the anode to the cathode.

Globulin dissolved in dilute alkali is, however, electro-negative, that is, moves in the opposite direction; in the presence of neutral salts, it is electrically inactive. Salts have a much smaller solvent power than acids or alkalis. The proteid of serum is inactive also, and further experiments suggest that only one and not several proteids are present in the serum. For quantitative results and complex physical deductions therefrom, the original paper must be consulted.

W. D. H.

Gaps in the Mixture Series in the Case of Isomorphous Substances. WILLEM STORTENBEKER (*Zeit. physikal. Chem.*, 1903, 43, 629—633).—According to van't Hoff, the similarity of solid solutions to liquid solutions is most marked in the case of isomorphous mixtures, miscibility being sometimes complete and sometimes limited. The author doubts whether this analogy holds, and discusses one or two pertinent cases.

There is a gap in the mixed crystal series for potassium and thallium nitrates (compare van Eijk, *Abstr.*, 1900, ii, 133), and as these substances are supposed to be isomorphous, they would furnish an example in support of van't Hoff's analogy. The author, however, maintains that they are not isomorphous, but isodimorphous; it is possible to get a solution of potassium nitrate which remains super-saturated in presence of a thallium nitrate crystal. It is suggested that potassium and thallium chlorates are also isodimorphous.

J. C. P.

Velocity of Solution of Solid Substances. LUDWIK BRUNER and STANISLAW TOLLOCZKO (*Zeit. anorg. Chem.*, 1903, 35, 23—40. Compare *Abstr.*, 1901, ii, 10; 1902, ii, 62).—Two new forms of apparatus in which a high velocity of rotation of the dissolving water can be attained are described. In one of these, the volume of the solvent can be varied and the other conditions maintained identical. Experiments were made with alabaster and with monoclinic gypsum crystals. The velocity of solution was found to be almost exactly proportional to the speed of rotation.

The volume of the solution has a very considerable influence on the velocity of solution. This is contrary to the conclusion already drawn by the authors (*Abstr.*, 1902, ii, 62), who now retract the deductions made from their erroneous conclusion. As the volume increases, the velocity of solution diminishes.

By the method previously used (*loc. cit.*), this influence has also been established.

Drucker's deduction (*Abstr.*, 1901, ii, 376) that the velocity of solution is a linear function of the time is not found to apply to alabaster, but the logarithmic function is applicable almost up to the point of saturation when the volume is constant ($s = 1/ft \cdot \log C/(C - x)$, where s is the velocity, f the surface of the solid, C the concentration of the saturated solution, and x the concentration at time t). The velocity of solution of the monoclinic gypsum is much smaller than that of alabaster, and this is attributed to the smoothness of the

surface. It was found that alabaster dissolved more slowly when polished than after the surface had become matt.

The logarithmic formula cannot truly represent the velocity of solution, since it does not take into account the volume. The authors deduce the same formula as Drucker (*loc. cit.*), containing the thickness of the layer of solution which adheres to the solid, and they calculate this to be 0.00051 cm.

It is proposed to define the velocity of solution as the absolute quantity dissolved in unit time (1 hour) from unit surface (1 sq. cm.) when a current, at constant velocity, of the solvent passes over the substance. For gypsum, this velocity is 0.312 (grams per hour).

J. McC.

Formation of Hydrates Deduced from Partition Coefficients. WILHELM VAUBEL (*J. pr. Chem.*, 1903, [ii], 67, 473—479. Compare Hantzsch and Vagt, *Abstr.*, 1902, ii, 8).—The partition coefficients were found to vary greatly with differences in the relative volumes of the two solvents in the following systems: phenol in water and benzene or carbon tetrachloride, *m*-cresol in water and ether, aniline in water and ether or carbon tetrachloride, *p*-toluidine in water and carbon tetrachloride. In these cases, the coefficient approaches constancy as the relative volume of the organic solvent is increased.

The author considers that abnormality of this kind may be ascribed to the formation of hydrates. The hydroxyl group alone cannot give rise to variation, as the coefficient was found to be independent of changes in the volumes of the solvents in the systems, resorcinol in water and ether, or benzene, or carbon tetrachloride.

G. Y.

Rate of Oxidation of Potassium Iodide by Chromic Acid. RALPH E. DELURY (*J. Physical Chem.*, 1903, 7, 239—253).—The rate of oxidation of potassium iodide by a mixture of potassium dichromate and sulphuric acid was studied. As a first approximation, the rate is proportional to the concentration of the dichromate and iodide, and to the square of that of the acid. The rate is actually somewhat less than proportional to the concentration of the dichromate and more than proportional to that of the iodide, being in the latter case reproduced by an expression, $R = mC + nC^2$, which may be explained by the assumption that two primary products of oxidation exist. The deviation in the case of the dichromate can be ascribed to decrease in the dissociation of the chromic acid on concentration. The addition of salts, with the exception of those of iron, has but little effect on the rate of the reaction, the temperature-coefficient of which is, moreover, considerably smaller than that which usually obtains, being about 1.4 per 10°.

L. M. J.

Trustworthiness of the Dissociation Constant as a means of Determining the Identity and Purity of Organic Compounds. HEYWARD SCUDDER (*J. Physical Chem.*, 1903, 7, 269—299).—It has been commonly assumed that the dissociation constant furnishes a trustworthy guide to the identity and purity of organic compounds. Thus a steady diminution of the constant at different dilutions has

been assumed to indicate the presence of isomerides or of acids of similar composition which could not be detected by analysis. The author has collected a large number of examples to show that the agreement between the values of the constant at different dilutions is not a trustworthy indication of the purity of the compound, as many cases occur in which the values change in dilution when there is no suspicion of impurity, and the value of the degree of dissociation is such that constancy would be expected. There is, moreover, much uncertainty regarding the actual values of the constant, and the author considers that for any compound a difference of 10 per cent. may be regarded as satisfactory agreement.

L. M. J.

Variation of Angles Observed in Crystals, especially of Potassium Alum and Ammonium Alum. HENRY A. MIERS (*Proc. Roy. Soc.*, 1903, 71, 439—441).—By allowing the image of a collimator slit to be reflected from the face of a crystal growing in an alum solution, and watching the displacements of this image, the changes in the inclination of each face during growth have been followed. It is found that each face of an octahedron of alum gives not one, but three images, and that the crystal has really the form of a very flat triakisoctahedron. Frequently one of the three nearly coinciding faces is large and the other two are very small. Further, the three images continually change their position during the growth of the crystal, the lines of movement, however, being inclined at 120° to each other. The images do not move continuously, but *per saltum*, from which it seems that the reflecting planes are vicinal faces, with rational but very high indices, inclined at definite angles to the octahedron face.

Similar observations have been made with sodium chlorate, zinc and magnesium sulphates, and the general conclusion is that the faces of a crystal consist of slightly inclined vicinal planes, which change their inclination with the growth of the crystal and with the depth of immersion. These vicinal faces are not due to concentration currents, since their angles (as shown in the case of alum) are unaffected by agitation of the liquid in which the crystal is growing. It is suggested that vicinal faces grow in preference to simple forms, because the crystallising material descends upon the growing face in a shower which is not very dense.

Experiments involving the determination of the refractive index of the solution have shown for alum, sodium chlorate, and sodium nitrate that the liquid in contact with the growing crystal is slightly supersaturated.

J. C. P.

Numerics of the Elements. III. EDMUND J. MILLS (*Phil. Mag.*, 1903, [vi], 5, 543—549. Compare Abstr., 1885, 344).—The atomic weights of the elements are of the form $y = pn - n(n/n + 1)^x$, where p is the number of the periodic group, $n + 1$ the number of periods in the system, and x a constant. The author shows that the values so calculated agree well with the latest values assigned to the atomic weights. He considers 15.94 to be the most probable value for the atomic weight of oxygen.

L. M. J.

Report of the International Atomic Weight Committee of 1903. KARL SEUBERT (*Zeit. anorg. Chem.*, 1903, 35, 45—47).—The author replies to Ostwald's remarks (*Zeit. physikal. Chem.*, 1903, 42, 634) on the publication of the Report issued by Clarke, Thorpe, and Seubert. J. McC.

Theory of Coloured Indicators. P. VAILLANT (*Compt. rend.*, 1903, 136, 1192—1195).—Ostwald and Nernst define an indicator as a weak acid or base, the molecule of which, RH or ROH, has a different colour from that of the ion, R. The author points out that if use is made of an acid indicator, RH, then in a solution of potassium hydroxide the comparatively large excess of alkali will condition that the salt RK is hardly dissociated, and the colour is due to this and not to the anion R. As a strong acid is added, the alkali is replaced by alkali salt, which is more highly dissociated, and consequently the number of K ions increases, and therefore RK remains in the state of undissociated molecules. When RK is transformed by the acid into RH, a certain number of R ions are produced, but as RH is a weak acid the dissociation is small and the colour of the solution will be due mainly to RH molecules. The older definition of an indicator (a weak acid or base the colour of which differs from that of its salts) seems, therefore, to be more correct.

In support of this view, a spectrophotometric examination was made of solutions of *p*-nitrophenol and of its potassium salt. *p*-Nitrophenol is colourless and its anion is coloured. The potassium salt in presence of excess of potassium hydroxide is coloured, and the colour is independent of the quantity of alkali present or of the potassium *p*-nitrophenoxide. Comparison of the absorption-coefficients a_λ show that the colour of potassium *p*-nitrophenoxide is the same as that of its anion.

It is indicated how these absorption-coefficients may be used for determining the degree of dissociation (hydrolytic) of the salt of the indicator, and how they may be employed for ascertaining the exact conditions of employment of a substance as indicator. J. McC.

Identification of Basic Salts. W. LASH MILLER and FRANK B. KENRICK (*J. Physical Chem.*, 1903, 7, 259—268).—The allocation of formulæ to basic salts is somewhat arbitrary, and much uncertainty exists regarding the nature of several such compounds. The authors point out that the phase law may give assistance in such cases. Thus, in a system of three components, if the composition of the precipitate varies whilst that of the solution remains constant, then the precipitate is a mixture of two phases; if the solution varies but the precipitate remains constant, then the precipitate is a chemical compound, whilst if both vary the precipitate is a single phase, but a solid solution. The method in which tests may be applied is indicated and the authors give a brief account of the results of a few experiments which have been carried out and which have indicated the existence of the following basic salts; $\text{PbCl}_2, 3\text{PbO}$; $2\text{SbCl}_3, 5\text{Sb}_2\text{O}_3$; $\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, 2\text{H}_2\text{O}$; $2\text{Bi}_2\text{O}_3, \text{N}_2\text{O}_5, \text{H}_2\text{O}$; $6\text{Bi}_2\text{O}_3, 9\text{N}_2\text{O}_5, 9\text{H}_2\text{O}$; $\text{CuCl}_2, 3\text{CuO}, 2\text{H}_2\text{O}$. L. M. J.

Cause of the Cementing Value of Rock Powders and the Plasticity of Clays. ALLERTON S. CUSHMAN (*J. Amer. Chem. Soc.*, 1903, 25, 451—468).—The cementing power of rock powders is a property similar to the plasticity of clays. If a rock powder be ignited at a temperature at which all the water of combination is expelled, the cementing power is invariably totally destroyed. Plastic powders moulded into briquettes under a given pressure suffer a certain compression, which is not shown by the material after the plastic condition has been destroyed by ignition. All rock powders with cementing properties resemble certain colloids which can be dehydrated and rehydrated until finally their structure is destroyed when the temperature is raised sufficiently high. A. McK.

Inorganic Chemistry.

Electrolytic Preparation of Persulphates. M. G. LEVI (*Zeit. Elektrochem.*, 1903, 9, 427—428).—The experiments were made without a diaphragm under the conditions which Müller and Friedberger (*Abstr.*, 1902, ii, 450) have found to be the best. The yield is unaffected by temperature up to 30°; it is almost independent of the nature of the cathode material, carbon, however, giving slightly better results than other materials; it is considerably affected by the physical condition of the platinum anode, a new smooth anode giving better results than an old rough one. T. E.

Distribution of Sulphur Dioxide between Water and Chloroform. JOHN McCRAE and WILLIAM E. WILSON (*Zeit. anorg. Chem.*, 1903, 35, 11—15).—At 20°, the distribution-coefficient of sulphur dioxide between water and chloroform varies with the concentration from 1.56 at a concentration of 0.055 gram-equivalent per litre in the aqueous phase to about 0.9 when the concentration is 1.038 gram-equivalents. The distribution-coefficient is, however, not directly proportional to the concentration.

Addition of hydrochloric acid diminishes the distribution-coefficient, and this is in agreement with the view that the inconstancy of the distribution ratio is due to the varying degree of electrolytic dissociation of the sulphurous acid. J. McC.

Preparation of Hyposulphites. PETER SPENCE & SONS, Ltd., & E. KNECHT (D.R.-P. 141452).—When solutions of sulphurous acid or sulphites and titanium sesquichloride are mixed, an orange coloration is produced, owing to the formation of hyposulphurous acid, which, however, rapidly decomposes. If the mixed solutions be allowed to flow into a solution of sodium hydroxide, the acid is converted into the comparatively stable sodium hyposulphite. The pre-

precipitated titanium hydroxide is filtered off, dissolved in hydrochloric acid, and again employed after conversion into the sesquichloride by electrolysis. C. II. D.

The Combustion of Carbon in Reductions by Calcium Carbide. FR. VON KÜGELGEN (*Zeit. Elektrochem.*, 1903, 9, 411—415).—Mixtures of chlorides and oxides of metals with calcium carbide (usually in the proportion $M''Cl_2 + 4M''O + CaC_2$) are heated in glass tubes in an atmosphere of nitrogen and the gases evolved collected and analysed. With lead salts, carbon dioxide alone is formed; with copper salts, about 11 per cent. of carbon monoxide is obtained, but this is reduced to 1.4 per cent. when the temperature of the reaction is diminished by admixture of sand. Replacement of the copper oxide by nickel oxide gives 5.2 per cent., and by tin oxide 16 per cent. of carbon monoxide. A mixture of zinc chloride and copper oxide gives carbon dioxide alone. These results confirm the theory of the reduction process previously given by the author (*Abstr.*, 1901, ii, 448). T. E.

Silicic Acid. II. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1903, 35, 16—22. Compare this vol., ii, 364).—The authors discuss the results of Graham and of Grimaux on colloidal solutions of silicic acid.

If a solution of sodium silicate is added to a dilute solution of hydrochloric acid, no precipitation takes place. If the solution be dialysed against water, the chlorine disappears in 1 to 3 weeks, but the sodium passes through the membrane much more slowly and only completely diffuses in 4 to 6 weeks. During the dialysis, a considerable proportion of the silicic acid also passes through the membrane. Gelatinous silicic acid separates from the dialysed solution as soon as the concentration reaches about 1 per cent. of silicon dioxide, but if a drop of acid or alkali be added, the solution may be evaporated until it contains about 10 per cent. of silicon dioxide before it gelatinises.

Silicic acid solution, obtained by the hydrolysis of ethyl silicate, is more stable in presence of acid or alkali than in pure water.

The results lead to the conclusion that the concentrated solutions of silicic acid are not pure, but probably contain a complex compound containing a preponderating amount of silica.

When silicic acid is digested with hydrochloric acid and then dried at 150° , it contains 1.5 per cent. of chlorine. It is presumed that a compound is formed which is stable at a high temperature but which decomposes readily in water.

The authors question if any of the so-called colloidal solutions are pure. J. McC.

Silicates. I. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1903, 35, 82—92).—From measurements of the conductivity of a dialysed solution of silicic acid to which increasing amounts of ammonia were added, it seems probable that the salts NH_4HSiO_3 and $(NH_4)_2SiO_3$ are produced, but the formation of $(NH_4)_3HSiO_4$ is doubtful.

By the action of salts of the alkaline earth metals on sodium silicate

solutions, salts of the type NaHBaSiO_4 are produced, but these are not quite pure, and when washed free from sodium the ratio of SiO_2 to BaO is greater than 1.

Barium, strontium, or calcium hydroxides dissolve silicic acid or act on a dilute solution of it and give microscopic crystals of the silicates $\text{BaSiO}_3 \cdot \text{H}_2\text{O}$, $\text{SrSiO}_3 \cdot \text{H}_2\text{O}$, and $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$ respectively.

It appears that in contact with water, silicates containing a higher proportion of alkaline earth oxide to silicon dioxide than 1 : 1 are not stable. Mixtures of $\text{M}(\text{OH})_2$ (2 mols.) ($\text{M} = \text{Ba}$, Sr , or Ca) and silicon dioxide (1 mol.) were well fused, then extracted with water; it was found that the water extracted the metallic hydroxide until the proportion of metallic oxide to silicon dioxide in the residue was 1 : 1.

J. McC.

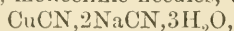
Attempt to Estimate the Relative Amounts of Krypton and Xenon in Atmospheric Air. Sir WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1903, 71, 421—426).—Of 191·1 kilograms of air passed through a Hampson liquefier, 11·3 were obtained in the liquid form. From this, after removal of oxygen and nitrogen, krypton and xenon were separated by fractional evaporation, the amounts actually obtained being 0·0028 gram and 0·0005 gram respectively. Hence there is present in air 1 part of krypton in 20 millions (by volume), and 1 part of xenon in 170 millions (by volume).

The pure krypton collected in the course of the investigation was employed for a redetermination of the density. The value obtained was 40·81 (compare the values 40·82 and 40·73, previously obtained).

J. C. P.

Double Salts of the Alkali Group. HERMANN GROSSMANN (*Ber.*, 1903, 36, 1600—1605).—From the behaviour of the alkali double fluorides formed from vanadium fluoride and oxyfluorides respectively, Ephraïm (this vol., ii, 418) draws the conclusion that, for all halogen double compounds, the number of molecules of alkali haloids which can combine with the haloid of a heavy metal falls with increasing atomic weight of the positive metal. The author points out, however, that this generalisation is not justifiable, since many cases are known where rubidium and caesium, in their behaviour in double salt formation, are allied, not to potassium, but to ammonium. The atomic volume of the various elements ought also to be considered.

Mercuric iodide dissolves readily in a cold aqueous solution of ammonium bromide, and the double salt, $2\text{HgI}_2 \cdot 3\text{NH}_4\text{Br}$, may be separated; it forms rhombic crystals and is decomposed by water into its components. From a hot aqueous solution of mercuric iodide in ammonium bromide, a salt of the composition $\text{HgI}_2 \cdot 2\text{NH}_4\text{Br}$ separates. Whilst a rubidium bromoiodide, $\text{HgI}_2 \cdot 2\text{RbBr}$, was easily prepared, the analogous potassium salt was not obtained. Mercuric sodium cyanide, $2\text{Hg}(\text{CN})_2 \cdot 2\text{NaCN} \cdot 3\text{H}_2\text{O}$, crystallises in long, prismatic needles. Two copper sodium cyanides were isolated. The one, $\text{CuCN} \cdot \text{NaCN} \cdot 2\text{H}_2\text{O}$, crystallises in colourless, monoclinic needles, the other,



is colourless, easily soluble, rhombic pyramids.

A. McK.

Electrolysis of Alkali Sulphides. ANDRÉ BROCHET and GEORGES RANSON (*Compt. rend.*, 1903, 136, 1134—1136. Compare Bartoli and Papasogli, *Abstr.*, 1883, 592; and Durkee, *Abstr.*, 1896, ii, 559).—Durkee's statement (*loc. cit.*) that solutions of alkali sulphides when electrolysed yield first thiosulphates and eventually sulphates is confirmed for dilute solutions. When concentrated solutions are employed at temperatures of from 50—70°, sulphur is produced at the anode and dissolves in the electrolyte forming polysulphides, whilst at the cathode, sodium is formed and hydrogen or hydrogen sulphide evolved.

The use of a diaphragm does not alter the course of the reaction, but in this case hydrogen sulphide alone is evolved. With dilute solutions of alkali sulphides, the anode must be constructed of platinum; when concentrated solutions containing sodium chloride are used, the anode may be of platinum, lead, or carbon, whilst in the absence of sodium chloride iron or nickel may also be employed. Copper, in all circumstances, behaves as a soluble electrode. During the experiments, the needles of the voltmeter and amperemeter oscillated regularly and in opposite senses, due to the continuous deposition of sulphur and its immediate solution from the anode (compare Kœlrichen, *Zeit. Elektrochem.*, 1901, 7, 629). T. A. H.

Decomposition of Lithium Carbonate by Heat. PAUL LEBEAU (*Compt. rend.*, 1903, 136, 1256—1257).—Lithium carbonate begins to decompose at about 600°, and the vapour tension of the lithium oxide is so high at this temperature that it may be completely volatilised. This dissociation of lithium carbonate distinguishes it from the carbonates of the alkali metals, and the volatility of the oxide produced assigns to lithium carbonate a different chemical rôle from that of the carbonates of the alkaline-earth metals. J. McC.

Preparation and Properties of Cæsium-ammonium and Rubidium-ammonium. HENRI MOISSAN (*Compt. rend.*, 1903, 136, 1177—1179).—Cæsium-ammonium of the formula NH_3Cs is formed when ammonia under atmospheric pressure acts on cæsium in the form of fine wire at 40°. On cooling by means of a mixture of acetone and solid carbon dioxide, a blue liquid is obtained from which the crystalline, brass-coloured, cæsium-ammonium separates. When brought into contact with the air, it takes fire. It dissolves in liquid ammonia to a blue, oily solution; if this solution be warmed or placed under reduced pressure, dissociation takes place and small crystals of cæsium are obtained.

Rubidium is not attacked by liquid ammonia at -75° , but at a slightly higher temperature action takes place, and a blue solution containing rubidium-ammonium, NH_3Rb , is formed. Rubidium is first attacked by gaseous ammonia at atmospheric pressure at -3° . The metal-ammonium easily dissociates and leaves small, prismatic crystals of rubidium.

The solutions of these metal-ammoniums in liquid ammonia have been used for the preparation of the carbides and acetylides of cæsium and rubidium. J. McC.

Some Properties of Colloidal Silver. ALLYRE CHASSEVANT and SWIGEL POSTERNAK (*Compt. rend. Soc. Biol.*, 1903, 89, 433—434).—Colloidal silver, prepared by Carey Lea's method and containing 90.08 per cent. of silver, becomes insoluble when kept, owing to absorption of atmospheric carbon dioxide by the ammonia retained by the silver; it is soluble in dilute ammonia solution and is reprecipitated by barium hydroxide, cupric sulphate, sodium or ammonium carbonate, and by acetic acid. The precipitate is soluble in excess of acetic acid without loss of its colloidal properties, and this solution, when electrolysed, deposits colloidal silver at the negative electrode, whilst from the ammoniacal solution, electrolysis leads to the deposition of colloidal silver at the positive electrode. These properties are characteristic of other colloidal substances (Posternak, *Abstr.*, 1901, ii, 544) and are not in harmony with Hanriot's view that colloidal silver is an ammonium salt of collargolic acid (this vol., ii, 368).
T. A. H.

Solubility of Gypsum in Solutions of Sodium Chloride. ALEXANDRE D'ANSELME (*Bull. Soc. chim.*, 1903, [iii], 29, 372—374).—The author has redetermined the solubilities of gypsum in solutions of sodium chloride of different concentrations, and obtained results which agree with those recorded by Cameron (*Abstr.*, 1902, ii, 75, 207) but differ from those given by Cloez (this vol., ii, 291).
T. A. H.

Electrolysis of Alkaline-earth Sulphides. ANDRÉ BROCHET and GEORGES RANSON (*Compt. rend.*, 1903, 136, 1195—1197).—When a concentrated solution of barium sulphide is electrolysed at 60—65°, sulphur, barium hydroxide, and hydrogen are formed. The sulphur forms polysulphides with the barium sulphide, and these are reduced by the hydrogen to sulphide and hydrogen sulphide. In dilute solution, sulphur, sulphite, thiosulphate, and sulphate are formed, and as these oxidised products are insoluble they are deposited on the anode.

The greater part of the remarks made in connection with the electrolysis of alkali sulphides (preceding page) apply also to barium sulphide. Platinum, iron, nickel, carbon, or lead may be used as anode. Copper behaves as a soluble anode. The addition of sodium chloride has no effect on the general course of the electrolysis, but if iron or nickel be used as electrodes they behave like soluble anodes. Increase of cathodic current density has little effect.
J. McC.

Electrolysis of Barium Sulphide with a Diaphragm. ANDRÉ BROCHET and GEORGES RANSON (*Compt. rend.*, 1903, 136, 1258—1260. Compare preceding abstract).—The primary action when barium sulphide solution is electrolysed with the electrodes separated by a diaphragm is the same as when no diaphragm is used; sulphur and polysulphides are formed at the anode, and the cathode chamber contains barium hydroxide, hydrogen being evolved at the cathode. The barium hydroxide diffuses into the anode compartment, but as it has

no action on the soluble polysulphides it may be recovered, since it separates on cooling the solution. The addition of barium chloride or an alkaline chloride to the solution seems to be without influence on the electrolysis, but an iron anode may not be used.

The electrolysis of barium sulphide solution offers a convenient method for the manufacture of barium hydroxide. J. McC.

Evaporation and Boiling of Metals in Quartz-glass and in the Electric Oven in the Vacuum of the Cathode-light. FRIEDRICH KRAFFT (*Ber.*, 1903, 36, 1690—1714).—The observation that many substances boil quite regularly and at a definite temperature under the pressure of a column of their own vapour only in the vacuum of the cathode-light can be extended to metals by using suitable apparatus. For this purpose, quartz vessels are invaluable, as they can be taken out from an electric furnace at 600° or 1200°, allowed to cool, and put straight back again without breaking, even when they contain metal, neither do they crack at the point at which the tube emerges from the furnace. They can be readily used for temperatures up to 1200°, and, with care, even at 1200—1400°. Tight joints can readily be made which will maintain the cathode-light vacuum, but as the vessels are attacked by oxides it is advisable to admit carbon dioxide or nitrogen rather than air when the vacuum is no longer needed. The use of an electric furnace is not only convenient, allowing as it does of a rapid and exact regulation of the temperature within 2° or 3° over a range from 14—1400°, but is, in fact, almost essential, as the quartz vessels do not project far from the furnace, and it is necessary that the wax which is used to make tight the joint should not be melted, as would inevitably be the case with any of the ordinary types of furnace.

In the vacuum of the cathode-light, zinc sublimes so rapidly, even at 300°, that the upper part of the vessel becomes covered with an opaque layer of metal in the course of a few seconds; actual boiling occurs when the temperature outside the tube is about 640°, and the process is very rapid, 5 grams being distilled in 30 minutes; in a large apparatus, it should be possible to distil a kilogram of zinc at constant temperature and in quite a short time. Cadmium begins to sublime at 322° and boils when the temperature of the oven is 474°. Selenium distils quickly at 380°, whilst tellurium begins to sublime at 430° and boils at 555°. Lead begins to evaporate at about 1000°, and at 1180° (temperature of oven) boils vigorously. Tin is much less volatile and does not show any sign of evaporating at 1100°. Antimony evaporates freely at 670° and rapidly distils at 775—780°. Bismuth begins to evaporate at 540° and boils at 1045—1050°. Silver evaporates very rapidly near its melting point, but does not boil at 1229°—the highest temperature of the experiment; a second experiment showed a very rapid evaporation at 1340°, but no boiling. Copper evaporates at about 1300°, but probably would not boil below 1500° or 1600°. Gold is even less volatile than copper and shows only a slight evaporation at 1375°; it might boil at about 1800°. It is notable that the boiling points are in the order of the valencies and not of the atomic weights of the metals.

The actual temperatures at which the metals boil depends on the

temperature of the oven and also on the height of the vapour column, which can be easily varied by raising or lowering the distilling tube in the furnace, since complete condensation takes place immediately outside the furnace. The boiling point of cadmium under a 6 cm. column of vapour rose from $424-450^{\circ}$ as the temperature of the oven was raised from $462-540^{\circ}$, under a 9–10 cm. vapour column from $435-470^{\circ}$ (oven temperature $488-583^{\circ}$), and under a 13–14 cm. column from $430-474^{\circ}$ (oven $485-589^{\circ}$); the boiling point thus rises regularly with the height of the vapour column, but only rises relatively slightly when the temperature of the oven is raised considerably. With the oven temperature at 714° , zinc boils at 545° under a vapour column of 60 mm., at 553° under 100 mm. of vapour, and at 560° under 135 mm. of vapour. With a furnace temperature of about 1100° , bismuth boils at 994° under 60 mm., at 1014° under 90 mm., and at 1045° under 135 mm. of vapour. Antimony under a short vapour column boils at 735° (oven $778-780^{\circ}$). Under a short vapour-column, lead boils at $1140-1142^{\circ}$ (oven 1226°), under 45 mm. of vapour at $1172-1173^{\circ}$ (oven 1225°).

T. M. L.

Solubility in Water of Chloride, Bromide, and Iodide of Lead. DAVID M. LIGHTY (*J. Amer. Chem. Soc.*, 1903, 25, 469–474).—The solubility in water of lead chloride, bromide, and iodide respectively was determined at temperatures ranging from 0° to 100° . The solubility of the iodide does not reach, even at 100° , the same value as that of the bromide at 0° . The solubility of the chloride at 0° is about $1\frac{1}{2}$ times that of the bromide; at 35° , they are equally soluble, whilst at 95° the solubility of the chloride is about three-fourths that of the bromide.

A. McK.

Combined Hydrogen contained in Reduced Copper. ANATOLE LEDUC (*Compt. rend.*, 1903, 136, 1254–1256).—In reply to Gautier's criticism (this vol., ii, 202), in which it is stated that the copper obtained from copper oxide by reduction with hydrogen does not retain hydrogen, the author describes an experiment in which it is conclusively proved that the copper retains a weighable quantity of hydrogen, thus confirming previous experiments (Abstr., 1891, 1422).

J. McC.

Alloys of Copper and Magnesium. OCTAVE BOUDOUARD (*Compt. rend.*, 1903, 136, 1327–1329. Compare this vol., ii, 78).—Confirmation of the existence of the compounds CuMg_2 , CuMg , and Cu_2Mg (*loc. cit.*) has been obtained by microscopic examination of alloys, prepared by the addition of magnesium to copper, fused under sodium chloride. Further, the compounds CuMg_2 and CuMg have been isolated by digesting in dilute hydrochloric acid (0.1 to 0.5 per cent.) for long periods metallic buttons, prepared by addition of the requisite quantities of magnesium to fused copper. The alloy, CuMg , has been obtained in an impure state by similar treatment.

T. A. H.

Action of Sodium Hyposulphite on Metallic Salts. OTTO BRUNCK (*Annalen*, 1903, 327, 240—250).—Sodium hyposulphite, the details of the preparation of the crystals of which from the commercial product are given in the paper, reduces various solutions of metallic salts.

On adding a solution of this salt to a solution of a copper salt, a precipitate is obtained which consists mainly of metallic copper and copper sulphide; the same substances are formed when the hyposulphite is in excess; in neither case was the presence of copper hydride demonstrated. Cupric chloride is at first completely reduced to the cuprous salt, which is then slowly converted into metallic copper. By this means, copper can be quantitatively separated from iron, zinc, nickel, and cobalt in neutral or acid solution.

Silver is completely precipitated, sulphur always being present in the precipitate. Gold is similarly reduced, a precipitate being formed in concentrated solutions, and a coloration in dilute solutions; in concentrations of 1 : 500,000, a pale rose coloration is produced.

When excess of sodium hyposulphite is added to a neutral solution of a zinc salt, zinc sulphide is precipitated.

From neutral solutions of cadmium, the *double salt*, $2\text{CdS}_2\text{O}_4 \cdot \text{Na}_2\text{S}_2\text{O}_4$, separates as a white, crystalline precipitate; from acid solutions, on the other hand, cadmium sulphide is thrown down. Mercury salts are reduced, finally, to the metal, which is converted into sulphide by excess of the hyposulphite.

K. J. P. O.

Action of Persulphates on Mercury. N. TARUGI (*Gazzetta*, 1903, 33, i, 127—133).—Mercury is readily attacked by solutions of persulphates, and especially so by an ammoniacal solution of ammonium persulphate. If the temperature of the reaction is not allowed to rise above 60° , the liquid deposits, on cooling, a *compound* in the form of white, acicular crystals arranged in radiating agglomerates and having the composition $\text{NH}_4 \cdot \text{S}_2\text{O}_8 \cdot \text{Hg} \cdot 2\text{NH}_3$; this substance, which is insoluble in nitric or sulphuric acid, but dissolves in hydrochloric acid and colours guaiacum tincture on heating, is also obtained by the action of ammonium persulphate on mercurous chloride. It is decomposed by water, yielding the ammonio-mercurous salt of Caro's acid and ammonium sulphate: $\text{NH}_4 \cdot \text{S}_2\text{O}_8 \cdot \text{Hg} \cdot 2\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4 \cdot \text{SO}_5 \cdot \text{Hg} + (\text{NH}_4)_2\text{SO}_4$.

The addition of water to the mother liquor remaining after the deposition of this compound causes the precipitation of an amorphous, white basic salt of the composition $2\text{NH}_4 \cdot \text{SO}_4 \cdot \text{Hg} \cdot 2\text{NH}_3 \cdot 3\text{Hg}_2\text{O}$.

T. H. P.

The Form in which Mercuric Iodide Dissolves. DESIRÉ GERNEZ (*Compt. rend.*, 1903, 136, 1322—1324. Compare Abstr., 1899, ii, 597; 1900, ii, 141; Kastle and Clark, Abstr., 1900, ii, 141; and Kastle and Reed, Abstr., 1902, ii, 234).—When solutions, prepared by dissolving red mercuric iodide in solid or liquid organic substances or in saline solutions, are induced to deposit the iodide either by evaporation (at temperatures below the transition point, 126° , of the red to the yellow form) or by cooling the solutions, the

yellow iodide invariably separates, even in presence of excess of the red form. This is the case even when the separation takes place at the temperature of liquid air. With solvents such as pyridine and quinoline, the red iodide combines, and on evaporation of such solutions there are obtained colourless additive compounds which, on further heating, are decomposed, leaving a residue of the yellow iodide.

T. A. H.

Mixed Crystals of Mercuric Iodide and Silver Iodide.

ALPHONSE STEGER (*Zeit. physikal. Chem.*, 1903, 43, 595—628).—When liquid mixtures of mercuric iodide (m. p. 257°) and silver iodide (m. p. 526°) are allowed to solidify, mixed crystals are formed in all cases, but there is a gap in the mixed crystal series from 5 to 20 molecular per cent. of silver iodide. The mixed crystals (α), containing from 0—5 molecular per cent. of silver iodide, are of the rhombic mercuric iodide type, those containing from 20—100 per cent. (β) are of the regular silver iodide type. Liquid mixtures with a composition between 5 and 20 per cent. of silver iodide solidify completely at 242° to a conglomerate of the 5 per cent. and 20 per cent. mixed crystals. At lower temperatures, the gap is wider, extending, for example, at 132° from 2 to 35 per cent. of silver iodide.

The transition temperature for the two forms of mercuric iodide is 127° , and it is remarkable that addition of silver iodide raises this point to 132° . All mixed crystal systems containing from 2 to 35 molecular per cent. of silver iodide are transformed at this temperature, the α crystals being replaced by others containing up to 10 per cent. of silver iodide.

Silver iodide has a transition point at 147° , but this temperature is lowered by addition of mercuric iodide; the lowest temperature thus reached is 135° for a mixture with 90 per cent. of silver iodide, and the mixed crystals formed by the transition contain very little mercuric iodide.

The mixed crystals (β) containing between 40 and 90 molecular per cent. of silver iodide undergo a change, the maximum temperature of which is 158° in a mixture with 66 molecular per cent. Apparently the mixed crystals (β) are then changed into the compound $\text{HgI}_2 \cdot 2\text{AgI}$, and the maximum temperature of this change is strictly analogous to the maximum freezing point of a pure compound. In mixed crystals (β) containing either more mercuric iodide or more silver iodide than is required for the compound, the temperature of change is lowered, on the silver iodide side to the point 135° , 90 molecular per cent., on the mercuric iodide side to the point 118° , 40 molecular per cent., these two being analogous to eutectic points on freezing curves. On neither side of the maximum, however, is the pure compound formed; according to the side, there is an admixture of silver iodide or mercuric iodide.

A further complication has been detected at low temperatures, inasmuch as the above-mentioned double salt undergoes a transformation at $50\text{--}45^{\circ}$, the colour changing from red to yellow.

J. C. P.

The Solubility of Aluminium in Nitric Acid. RUDOLPH Woy (*Zeit. öffentl. Chem.*, 1903, 9, 158—161).—Aluminium plates, used instead of lithographic stones in a certain printing works, were found to be strongly corroded by the nitric acid employed for cleaning the plates. As the nitric acid was free from hydrochloric acid, a number of experiments were undertaken to ascertain the action of pure nitric acid on metallic aluminium. It was found that, contrary to the statements in some text-books, the acid has a considerable solvent action, depending at the ordinary temperature on the concentration of the acid. The acid solution, as the reaction proceeds, becomes charged with ammonium salts and a filmy precipitate of carbide or silicide separates, aluminium nitrate also being formed. A solution containing 10 grams of HNO_3 in 100 c.c. of water dissolved about 1 per cent. from an aluminium plate measuring 5 cm. by 3.5 cm. in $2\frac{1}{2}$ days, and in 55 days, 20 per cent. With a solution containing 30 grams of HNO_3 per 100 c.c., 3 per cent. of the plate dissolved in $2\frac{1}{2}$ days and 56 per cent. in 55 days. The latter solution dissolved 2.5 per cent. in 10 minutes at 100° . These results were obtained with ordinary technical aluminium and not with the chemically pure metal.

W. P. S.

Cementation of Steels. LÉON GUILLET (*Compt. rend.*, 1903, 136, 1319—1321).—The rate of penetration of steel by carbon is independent of the amount of carbon originally present in the steel, but depends on the nature of the carburising material employed and the temperature at which the operation is conducted; the maximum absorption is independent of the two latter conditions. Commercial wood charcoal containing small quantities of potassium carbonate attains the maximum rate of penetration in one hour at 1000° , and the minimum rate after 8 hours at the same temperature, but with wood charcoal to which 5 per cent. of the carbonate has been added, the maximum rate of penetration is attained only after 8 hours at 1000° .

Cementation experiments with this mixture in a current of nitrogen or ammonia afford no support to the view that the accelerating effect of potassium carbonate is due to the initial formation of potassium cyanide.

The brittleness of "super-carbonised" steels is partly due to the influence of high temperature on the internal structure of the metal and partly to the formation of acicular crystals of cementite. When steel is heated at 1100° for 8 hours with carburising materials, the amount of carbon absorbed varies from 1.77 to 1.98 per cent., depending on the nature of the material employed. If the heating be continued beyond this point, the needles of cementite are replaced by ill-defined granular masses, and a period of slow absorption begins; the formation of cementite continues, and ultimately a zone of this substance is formed, the content of carbon slowly increasing until after 75 hours at 1000° the steel contains 3.82 per cent. When a steel containing 0.120 per cent. of carbon and 7 per cent. of nickel is carburised until the outer layers contain 0.80 per cent. of carbon, the original perlite is replaced by martensite; an effect similar to that

produced by tempering (this vol., ii, 297). Non-magnetic steels (in which the iron is in the γ -state) containing 25—30 per cent. of nickel and 0.11 to 0.81 per cent. of carbon were found to be carburised by heating at 450° in a bath of potassium cyanide with chlorides of the alkali and alkaline-earth metals, whilst a steel free from nickel and containing 0.140 per cent. of carbon did not undergo cementation under these conditions.

T. A. H.

Decarburisation of Steel and of Thin Metallic Plates by Evaporation under Reduced Pressure. G. BELLOC (*Compt. rend.*, 1903, 136, 1321—1322. Compare this vol., ii, 297).—When steel wire is heated in porcelain tubes containing air, carbon dioxide is formed, whilst in hydrogen, saturated hydrocarbons are produced; in both cases, decarburisation of the steel takes place. In the absence of gases occluded by the steel, these changes do not occur.

When steel is heated under reduced pressure, a portion of the wire is volatilised and the remainder becomes super-carburised (*loc. cit.*). This volatilisation is retarded by the presence of a layer of oxide on the surface of the steel and is inhibited if the tube containing the steel be heated externally.

Under the same conditions, copper, nickel, and silver furnish respectively greenish-bronze, maroon, and blue sublimates of the metals.

T. A. H.

The Rusting of Iron and its Passivity. MARTIN MUGDAN (*Zeit. Elektrochem.*, 1903, 9, 442—455).—Weighed pieces of iron wire are placed in solutions through which air, free from carbon dioxide, is passed. After removing the rust, the iron is again weighed, the loss giving the rate of action. The attack appears to set out from points in the iron, and the velocity of rusting therefore varies considerably with the number of such points which happen to exist in the sample used. The variations are, however, not large enough to conceal the effect of the nature of the salt used in the solution. The chlorides of the alkalis, ammonium, and the alkaline earths accelerate rusting to about the same extent. Bromides, sulphates, and perchlorates are nearly equally active, potassium nitrate somewhat less so, and pure water less still. Iron remains practically unattacked in solutions of potassium (or sodium) chlorate, bromate, iodate, chromate, dichromate, acetate, oxalate, tartrate, ferro- and ferri-cyanides, cyanide, hydrogen carbonate, borate, hydroxide, and ammonia (compare *Proc.*, 1903, 19, 150, 157).

Steel behaves very much like soft iron, whilst cast iron always shows a greater tendency to rust.

The order in which iron is attacked in these solutions is not changed by adding small quantities of acid, or of alkali, or of oxidising agents such as hydrogen peroxide, potassium ferricyanide, or sodium hypobromite, although the rate of rusting is increased or diminished. Solutions containing a mixture of salts possess properties intermediate between those of solutions of the pure salts; thus, addition of salt to a solution of sodium hydroxide causes iron immersed in it to rust, although more slowly than in an equally concentrated solution of pure salt.

The potential of iron immersed in the solutions is measured and found to vary considerably with the nature of the dissolved salt. Since the dissolved salts cannot be supposed (as the author shows) to take part in the reaction, this should not be the case. The phenomena can only be regarded as further instances of a metal assuming a more or less "passive" condition. The measurements show that iron in solutions of chlorides, bromides, iodides, fluorides, sulphates, perchlorates, nitrates, and acids is at a higher potential than a hydrogen electrode in the same solution, whilst the salts of weak anions (chlorate, acetate, hydroxide, cyanide, chromate, and permanganate) give potentials much below that of the hydrogen electrode in the same solution, or in the first case iron can dissolve, eliminating hydrogen, whilst the reverse would occur in the second case. The different potentials show that the rusting in one case and not in the other is due to some modification of the iron impressed on it by contact with the solution.

The fact that many of the salts, in solutions of which the iron is not attacked, are reducing agents, speaks against the passivity being due to a layer of oxide.

The passivity varies in degree with the solution used, and it is apparent in other reactions than rusting as, for example, in the precipitation of silver or copper from solutions of their salts. Salts containing the anions which make the iron passive are not decomposed.

The passivity is retained for some time. This can be shown by a solution of $\text{AgNO}_3(0.03N) + \text{KClO}_3(0.06N)$. A fresh iron wire or one soaked in sodium chloride solution precipitates silver from this solution in five minutes, a wire soaked in sodium acetate solution requires half an hour, one soaked in sodium hydroxide solution still longer, whilst a wire made passive in concentrated nitric acid remains for hours without action.

T. E.

Some Physical Properties of Nickel Carbonyl. JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1903, 71, 427—439).—Mond, Langer, and Quincke found that nickel carbonyl vapour exploded at 60° with a flash of light, carbon dioxide being detected among the products of decomposition. The authors show that this explosive decomposition does not take place in presence of an inert gas, and they have accordingly determined the vapour density of nickel carbonyl by Victor Meyer's method in atmospheres of hydrogen, nitrogen, and ethylene at temperatures between 63° and 216° . An atmosphere of carbon monoxide was also used in order to study the influence of the gaseous product of the dissociating nickel carbonyl. The vapour density is greater in ethylene than in nitrogen or hydrogen, and greatest in the carbon monoxide atmosphere. In the last gas, the vapour density is nearly normal at 100° , and even at 182° the dissociation is incomplete, whilst in nitrogen dissociation is practically complete at 155° . In order to study the dissociation of the undiluted vapour, determinations of the density were made by Hofmann's method up to 182° , at which temperature dissociation was practically complete.

The temperatures at which the meniscus of nickel carbonyl dis-

appeared and reappeared in a sealed tube varied from 191° to 195° in different experiments, and, allowing for the effect of the carbon monoxide present, the authors estimate that the true critical temperature is about 200° . The critical pressure was found to be about 30 atmospheres.

The vapour pressure of nickel carbonyl has been determined by a statical method at points between -9° and $+30^{\circ}$, and the relation between the vapour pressure p and the absolute temperature T is given by the formula $\log p = 7.355 - 1415/T$. From this, the boiling point is calculated to be 43.2° , and an actual determination of the boiling point of some carefully purified nickel carbonyl gave the value $43.2-43.3^{\circ}$ (under 769 mm. pressure). Tested in this way, the authors' vapour pressure curve is more accurate than that given by Mittasch (Abstr., 1902, ii, 307).

Extrapolation of the above formula to 200° gives $p = 30.4$ atmospheres (compare the value of the critical pressure recorded above).

Experiments are also described which demonstrate simply the dissociation of nickel carbonyl and the reversibility of the action (compare Mittasch, *loc. cit.*).
J. C. P.

Chromium Silicides. PAUL LEBEAU and J. FIGUERAS (*Compt. rend.*, 1903, 136, 1329—1331).—When a mixture of chromium, copper, and a small quantity of silicon is melted together (Abstr., 1901, ii, 317) and the resulting button is digested in nitric acid, there remain as a residue, prismatic crystals of the silicide, SiCr_3 (Zettel, Abstr., 1898, ii, 520). Using larger quantities of silicon, the silicide, SiCr_2 , in lozenge-shaped crystals with brilliant facets, is obtained (Moissan, Abstr., 1896, ii, 174), whilst with still larger proportions of silicon the *silicide*, Si_2Cr_3 , is produced, and eventually the compound Si_2Cr (de Chalmot, Abstr., 1897, ii, 214).

The chromium silicide, Si_2Cr_3 , is best prepared by fusing in the electric furnace a mixture of copper silicide (100 grams) and chromium (4 grams), and digesting the resulting mass alternately with nitric acid (50 per cent.) and solution of sodium hydroxide (10 per cent.). It crystallises in long, quadratic prisms, has a sp. gr. 5.6 at 0° , abrades glass, but not quartz, and is stable in moist or dry air at the ordinary temperature, but oxidises superficially at 1100° . The silicide becomes incandescent when placed in chlorine at 400° , forming silicon and chromic chlorides; it reacts slowly with bromine at a red heat, but is not acted on by iodine. It is insoluble in dilute hydrochloric acid, but chromous chloride is formed by solution of the silicide in the warm concentrated acid or by the action of gaseous hydrogen chloride. It is attacked by hydrofluoric but not by sulphuric or nitric acid. Fused potassium chlorate or nitrate does not attack the silicide, but it is converted by fused alkali carbonates into the silicate and chromium sesquioxide, and by fused mixtures of alkali carbonates and nitrates into the silicate and chromate.

The silicides of chromium are not analogous in composition to those of iron, cobalt, manganese, or nickel; the silicides of nickel are difficult to isolate owing to their ready decomposition by acids.

T. A. H.

Constitution of Vanadium Double Fluorides. FRITZ EPHRAIM (*Zeit. anorg. Chem.*, 1903, 35, 80—81).—Melikoff and Kasanezky (*Abstr.*, 1902, ii, 27) have deduced from the action of hydrogen peroxide on potassium vanadium fluoride that the constitution of this compound is $\text{VF}_3(\text{OK})_2$, and that the potassium is not directly united to fluorine. At the same time, however, they have shown that the ammonium salt, $3\text{NH}_4\text{F} \cdot \text{VO}_2\text{F}$, to which they attribute the constitution $\text{VF}_3(\text{ONH}_4)_2 \cdot \text{NH}_4\text{F}$, behaves quite similarly, although it does contain ammonium directly united to fluorine. Although the constitutions deduced by Melikoff and Kasanezky may be correct, the author does not regard the oxidation experiments as proving that they are so.
J. McC.

Action of Hydrochloric Acid on Vanadic Acid. Preparation of Double Compounds of Vanadium Pentoxide containing Chlorine. FRITZ EPHRAIM (*Zeit. anorg. Chem.*, 1903, 35, 66—79).—When hydrogen chloride is passed over a warm mixture of vanadic acid and a dehydrating agent (phosphoric oxide or zinc chloride), vanadium oxychloride, VOCl_3 , is formed, and can be condensed to a yellow oil. In moist air, the oxychloride gives rise to red fumes. The method of separating vanadium from the alkali metals by heating in a current of hydrogen chloride, described by Smith and Hibbs (*Abstr.*, 1894, ii, 455), is based on the formation of this oxychloride. The brown colour of solutions of vanadium pentoxide in concentrated hydrochloric acid is due to the formation of vanadium oxychloride.

When vanadic acid is fused with potassium chloride, reduction takes place and chlorine is liberated. From various fusions, the following polyvanadates have been isolated: $\text{K}_2\text{O}, 2\text{V}_2\text{O}_5, 4\text{H}_2\text{O}$ as golden-yellow crystals; $\text{K}_2\text{O}, 2\text{V}_2\text{O}_5, 6\text{H}_2\text{O}$ as brown rhombohedra;

$11\text{K}_2\text{O}, 12\text{V}_2\text{O}_5, 3\frac{1}{2}\text{H}_2\text{O}$
as greyish-yellow, hard, cubical crystals; and $11\text{K}_2\text{O}, 12\text{V}_2\text{O}_5, 3\text{H}_2\text{O}$ as long needles.

When the chlorides of calcium, magnesium, or iron (ferrie) are added to solutions of vanadium double fluorides, reaction takes place according to the equation: $2\text{KF} \cdot \text{VO}_2\text{F} + \text{CaCl}_2 = \text{CaF}_2 \cdot \text{VO}_2\text{F} + 2\text{KCl}$. The new double fluorides then react with more chloride to produce double chlorides according to the equation: $2[\text{CaF}_2 \cdot \text{VO}_2\text{F}] + 3\text{CaCl}_2 = 2[\text{CaCl}_2 \cdot \text{VO}_2\text{Cl}] + 3\text{CaF}_2$, and these double chlorides at once decompose with water: $\text{CaCl}_2 \cdot \text{VO}_2\text{Cl} + 2\text{H}_2\text{O} = \text{CaO} \cdot \text{VO}_2(\text{OH}) + 3\text{HCl}$. When a solution of vanadium fluoride is added to excess of barium chloride solution, a light yellow, flocculent precipitate of *barium vanadium fluoride*, $\text{BaF}_2 \cdot \text{VO}_2\text{F}$, is formed.

Reaction takes place between fused potassium fluoride and vanadic acid according to the equation: $6\text{KF} + \text{V}_2\text{O}_5 = 2[2\text{KF} \cdot \text{VO}_2\text{F}] + \text{K}_2\text{O}$.
J. McC.

Bismuth Alkali Thiosulphates. OTTO HAUSER (*Zeit. anorg. Chem.*, 1903, 35, 1—10).—The observations of Carnot (*Abstr.*, 1876, 420) have been in the main confirmed.

Bismuth sodium thiosulphate, $\text{Na}_3\text{Bi}(\text{S}_2\text{O}_3)_3$, is formed when bismuth

nitrate is rubbed with excess of sodium thiosulphate. The mixture is extracted with a mixture of alcohol and water (1 : 1); on addition of more alcohol, the salt is precipitated as a yellow oil, which, when placed over sulphuric acid under reduced pressure, gives orange-yellow crystals. The salt is unstable in the dry state, but keeps fairly well in alcoholic aqueous solution.

When a solution of potassium chloride and one of sodium thiosulphate is added to a cooled solution of bismuth oxide in hydrochloric acid, yellow, prismatic crystals of *bismuth potassium thiosulphate*, $K_3Bi(S_2O_3)_3 \cdot \frac{1}{2}H_2O$, separate. One hundred c.c. of solution saturated at 2° contain 3.5 grams of the salt, and at 18° about 7 grams. The aqueous solution rapidly decomposes, but solutions containing alkali salts are stable. Sodium thiosulphate solution dissolves more of the salt than pure water does. The thiosulphate group in the salt cannot be titrated with iodine. The precipitation of this salt may be used for the detection of potassium, but cannot serve for its quantitative estimation. In a vacuum over phosphoric oxide, the anhydrous salt, $K_3Bi(S_2O_3)_3$, is formed.

Yellow *bismuth rubidium thiosulphate*, $Rb_3Bi(S_2O_3)_3 \cdot \frac{1}{2}H_2O$, is formed in the same way as the potassium salt. It forms a yellow, crystalline powder which loses its water of crystallisation over phosphoric oxide in a vacuum. When this yellow salt is treated with a small quantity of ice-water, it becomes brown with formation of the salt $Rb_3Bi(S_2O_3)_3 \cdot H_2O$.

When sodium thiosulphate is mixed with a solution containing caesium nitrate and bismuth nitrate in nitric acid and then alcohol added, a yellow, crystalline powder of *bismuth caesium thiosulphate*, $Cs_3Bi(S_2O_3)_3$, is deposited. It is more stable than the potassium or rubidium salts.

Bismuth barium thiosulphate, $Ba_3[Bi(S_2O_3)_3]_2$, is formed in the same way as the potassium salt; it is hydrolysed very easily.

It has been proved that the solutions of these various salts contain the complex anion $Bi(S_2O_3)_3'''$, which, however, breaks up comparatively easily.

J. McC.

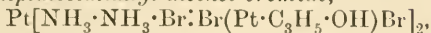
Platinum Compounds. EINAR BILLMANN and A. C. ANDERSON (*Ber.* 1903, 36, 1565—1571).—Potassium platinosobromide, $K_2PtBr_4 \cdot 2H_2O$ (compare Thomsen, this Journal, 1877, ii, 276), may be obtained by reducing the platinibromide with normal potassium oxalate at 100° ; about fifty per cent. separates, when the solution is concentrated, in the form of large, black, rhombic crystals [$a:b:c = 0.60582:1:0.70499$]. The remainder is best transformed back into the platinibromide by the addition of bromine. The platinosobromide is readily soluble in water, and when its solution is boiled for some time decomposition occurs. With platodiammine nitrate, it yields a sparingly soluble Magnus' salt, $Pt(NH_3)_4PtBr_4$, which has an intense green colour.

Allyl alcohol reacts with the platinosobromide yielding potassium bromide and *potassium platosemiallyl alcohol bromide*,



(compare Abstr., 1900, i, 543), the latter in the form of dark red, prismatic crystals.

Platodiammineplatosemiallyl alcohol bromide,



forms a yellow, crystalline powder consisting of felted needles which are decomposed when boiled with water. *s*-Platosammine chloride (platosemidiammine chloride) may be readily prepared by Jörgensen's method (Abstr., 1900, i, 542), or by the action of ammonium oxalate on ammonium platinichloride.

J. J. S.

Mineralogical Chemistry.

[Montanite from New South Wales.] JOHN C. H. MINGAYE (*Ann. Rep. Dep. Mines, N.S.W.*, for 1901, 1902, 172, 184).—The mineral is massive and contains a few specks of unaltered tetradymite; it is from the Nanima bismuth mine near Yass; sp. gr. 6.823. Analysis gave:

Bi.	Te.	Se.	Fe.	Cu.	Mn.	MgO.	CaO.
57.73	19.15	trace	0.40	0.24	1.78	0.08	trace
	Insol.	CO ₂ .	H ₂ O.	O.	Total.		
	2.52	1.05	1.61	[15.44]	100.00.		

L. J. S.

Identity of Simonyite with Astrakanite [Blödite]. F. M. JAEGER (*Tsch. Min. Mitth.*, 1903, 22, 103—108).—Crystals of the so-called simonyite from Hallstadt, Upper Austria, agree in their interfacial angles and optical characters with blödite. Half the water is expelled at 120°, but in this respect both blödite and "simonyite" seem to show some variation.

L. J. S.

Celestite from Tunis. PIERRE TERMIER (*Bull. Soc. franç. Min.*, 1902, 25, 173—180).—A crystallographic description is given of the celestite which occurs associated with zinc ores in Triassic limestones at Jebel Kebbouch and Jebel Bezina. Analysis, by Pisani, of material from the first-named locality gave:

SO ₃ .	SrO.	CaO.	Total.
43.49	56.20	0.40	100.00

L. J. S.

Minerals from Leona Heights, Alameda Co., California. WALDEMAR T. SCHALLER (*Bull. Dep. Geol. Univ. California*, 1903, 3, 191—217).—The pyrites-ore of the Alma mine contains some chalcopyrite; its alteration has given rise to the various secondary sulphates described below and to hæmatite and limonite. Melanterite occurs as an efflorescence and as small crystals, but only in small

quantities; an approximate analysis gave the results under I. Pisanite, as blue, transparent crystals, is the most abundant secondary mineral; analysis gave the results under II—IV (after deducting pyrites, which is intergrown with and encrusted on the pisanite); in II, $\text{Fe} : \text{Cu} = 1 : 1$, and in III, $2 : 1$; sp. gr. $1.8-1.9$. *Boothite* is the name given to a new copper sulphate which differs from chalcantite in containing $7\text{H}_2\text{O}$ instead of $5\text{H}_2\text{O}$; it occurs in crystalline masses, rarely in crystals, of a blue colour, perhaps slightly paler than that of chalcantite, with which it is intimately associated; sp. gr. 2.1 . On exposure to air, it becomes white; it is readily soluble in water. Analysis of fibrous and massive material gave the results under V and VI respectively. Boothite is monoclinic and isomorphous with melanterite and pisanite, as shown in the following table:

	$a : b : c$	β
Melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$...	$1.1828 : 1 : 1.5427$	$75^\circ 44'$
Pisanite, $(\text{Fe}, \text{Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O}$...	$1.1670 : 1 : 1.5195$	$75^\circ 30'$
Boothite, $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$...	$1.1622 : 1 : 1.5000$	$74^\circ 24'$

In all these minerals, $6\text{H}_2\text{O}$ is lost at $200-250^\circ$; the presence of one molecule of constitutional water suggests that they are salts of tetrahydroxysulphuric acid, $\text{SO}(\text{OH})_4$.

Chalcantite occurs abundantly as pale blue crystals or green, drusy coatings on the ore and on the timbers of the mine, and as dark blue, loose crystals; analysis VII. Copiapite is abundant as yellow, granular masses; analysis VIII. Epsomite as fibrous efflorescences; analysis IX. Chalcantite and epsomite also lose all their water, except one molecule, at $100-110^\circ$; they also can be expressed as salts of tetrahydroxysulphuric acid; copiapite, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 4\text{H}_2\text{O} + 14\text{H}_2\text{O}$, is also a salt of the same acid.

Crystallographic descriptions of each of these minerals are given, and several new forms recorded. The probable occurrence of alunogen is also noted.

	CuO.	FeO.	Fe_2O_3 .	Al_2O_3 .	MgO.	SO_3 .	H_2O .	Total.
I.	nil	28.1	—	—	nil	31.2	42.0	101.3
II.	15.73	12.31	—	—	—	28.21	45.14	101.39
III.	9.22	16.47	—	—	—	29.18	45.74	100.61
IV.	17.95	5.46	—	—	2.82	29.25	45.21	100.69
V.	27.83	trace	—	—	trace	28.37	44.06	100.26
VI.	28.53	0.28	—	—	trace	28.65	43.76	101.22
VII.	31.14	nil	—	—	trace	32.06	35.70	99.71*
VIII.	—	0.44	25.04	0.31	0.29	38.36	29.71	99.58†
IX.	nil	nil	—	trace	14.8	31.7	53.0	99.5

* Insoluble, 0.81.

† Insoluble, 5.43.

L. J. S.

Palacheite. ARTHUR S. EAKLE (*Bull. Dep. Geol. Univ. California*, 1903, 3, 231—236).—This new mineral is of recent formation in the old workings of the Redington mercury mine, Knoxville, California, where it is found as loosely coherent aggregates of minute, monoclinic

crystals. The crystals are deep brick-red and strongly pleochroic ; streak, yellow. There is a perfect cleavage parallel to the plane of symmetry. Goniometric and optical determinations are given. Sp. gr. 2·075. The following analytical results correspond with the formula $\text{Fe}_2\text{O}_3, 2\text{MgO}, 4\text{SO}_3, 15\text{H}_2\text{O}$:

Fe_2O_3 .	MgO.	SO_3 .	H_2O .	Total.
19·51	9·35	38·37	32·28	99·51

$9\text{H}_2\text{O}$ (19·53 per cent.) is lost at 100° , $13\text{H}_2\text{O}$ at 270° , and the remainder at about 300° . The new mineral appears to be closely allied to the imperfectly characterised rubrite (Abstr., 1898, ii, 437).

L. J. S.

Babingtonite from Somerville, Massachusetts. CHARLES PALACHE and F. R. FRAPPIÉ (*Proc. Amer. Acad. Arts and Sci.*, 1902, 38, 383—393).—A detailed crystallographic description is given of the small, brilliant, black crystals of babingtonite, which occur with prehnite, quartz, epidote, calcite, &c., in veins in diabase at Somerville. Analysis of finely granular material embedded in prehnite gave :

SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO.	MnO.
52·25	0·18	5·27	7·49	11·05	1·94
CaO.	MgO.	$(\text{K}, \text{Na})_2\text{O}$.	H_2O .	Total.	
20·36	0·46	0·22	0·29	99·51	

These results agree with the formula $5\frac{3}{4}\text{R}''\text{SiO}_3, \text{R}_2'''(\text{SiO}_3)_3$.

Babingtonite from Athol, Massachusetts, is also described.

L. J. S.

Meteoric Iron from Rafrüti, Switzerland. EMIL W. COHEN (*Mitth. naturw. Ver. Neu-Vorpommern u. Rügen*, 1903, 34, 84—88).—This iron, found at Rafrüti, in Emmenthal, Canton Bern, is finely granular in structure ; sp. gr. 7·596. Analysis gave :

Fe.	Ni.	Co.	Cu.	Cr.	C.	P.	S.	Total.
89·87	9·54	0·61	0·03	0·01	0·18	0·06	0·11	100·41

L. J. S.

Meteoric Iron from Cuernavaca, Mexico. EMIL W. COHEN (*Mitth. naturw. Ver. Neu-Vorpommern u. Rügen*, 1903, 34, 98—102).—The meteoric iron from Cuernavaca, Morelos, Mexico, is an octahedrite with fine lamellæ ; sp. gr. 7·748. Analysis by O. Hildebrand gave :

Fe.	Ni.	Co.	Cu.	Cr.	P.	S.	Total.
89·70	8·76	1·19	0·05	0·00	0·33	0·12	100·15

A brief description is also given of the meteoric iron from Fredell, Bosque Co., Texas.

L. J. S.

Meteoric Iron from Mukerop, Great Namaqualand. ARISTIDES BREZINA and EMIL W. COHEN (*Jahresb. Ver. Naturk. Württemberg*, 1902, 58, 292—302).—This mass of iron, weighing 178 kilograms, was found in 1899 at Mukerop, in the Gibeon district, Great Namaqualand. The structure is octahedral, with fine lamellæ. The mass is remarkable in consisting of two large individuals orientated in twinned position with respect to each other, the twin-plane being a face of the octahedron. Moreover, in a portion of one of these individuals the structure is so fine that, to the naked eye, the iron appears to be compact. Another peculiarity of the mass is that it is penetrated by plane fissures parallel to the faces of the octahedron. Sp. gr. 7.783. Analyses (I by O. Hildebrand, and II by Fraas) gave the following results; after deducting the variable accessory constituents—schreibersite, troilite, and lawrencite—the composition of the nickel-iron is practically identical in both analyses:

	Fe.	Ni.	Co.	Cu.	Cr.	C.	Cl.	S.	P.	Insol.	Total.
I.	90.96	8.19	0.46	0.04	0.02	0.02	0.01	trace	0.18	0.01	99.89
II. [91.371]	7.97	0.50	0.016	0.035	0.05	not det.	0.024	0.034	—	—	100.00

In structure and chemical composition, this iron resembles those of Bethany (Abstr., 1900, ii, 736) and Lion River, also from Great Namaqualand, and all may possibly belong to the same fall.

L. J. S.

Reed City Meteorite. H. L. PRESTON (*Proc. Rochester (N.Y.) Acad. Sci.*, 1903, 4, 89—91; *J. Geol.*, 1903, 11, 230—233).—This iron, weighing 19.8 kilograms, was found in 1895 near Reed City, Osceola Co. Michigan. The structure is octahedral, with well-marked Widmanstätten figures. A partial analysis gave: Fe, 89.386; Ni, 8.180 per cent. Sp. gr. 7.6.

L. J. S.

Physiological Chemistry.

Influence of Compressed Air on Respiratory Exchange. LEONARD HILL and J. J. R. MACLEOD (*J. Physiol.*, 1903, 29, 492—510).—Air under 4 atmospheres pressure or upwards markedly diminishes the output of carbon dioxide and water in mice, and increases the loss of body heat. Oxidation processes are lessened. The output of water is lessened, because moist air, when compressed, becomes saturated with aqueous vapour and delays evaporation by hindering the diffusion of the vapour. The escape of aqueous vapour per litre varies inversely as the pressure in the chamber. The loss of body heat is due to the increased conductivity of dry compressed air and of air saturated with aqueous vapour. Moist air under 1 atmosphere and 20° increases tissue combustion in mice by increasing the loss

of heat. The loss may be greater than the gain, so that the mice are cooled and may even die when exposed for a long time to a current of moist air below 20°.

W. D. H.

Influence of Compressed Air and Oxygen on the Blood Gases. LEONARD HILL and J. J. R. MACLEOD (*J. Physiol.*, 1903, 29, 382—387).—The amount of nitrogen in the blood varies according to Dalton's law, but the process of saturation is a long one, occupying about $1\frac{1}{2}$ hours. This explains the fact that visitors to caissons who remain there only a few minutes are not affected. The results with oxygen are not so conclusive, but point to absorption of this gas by the plasma. On de-compression, the liberation of gas bubbles is limited to the venous blood. The amount of carbon dioxide in the blood is lessened; the diminution of this gas in the expired air is therefore probably due to lessened oxidation.

W. D. H.

Antitryptic Action of the Blood. KARL GLAESSNER (*Beitr. chem. Physiol. Path.*, 1903, 4, 79—86).—The antitryptic action of the blood differs for the blood sera and trypsins of different animals. It is strongest against the trypsin of the same species. This action is associated with the euglobulin fraction of serum proteids. The quantity increases in the blood during digestive activity, and this appears to serve the purpose of destroying any trypsin which may be absorbed.

W. D. H.

Influence of Alkalis on the Alkalinity of the Blood. JOSEPH WEISS (*Zeit. physiol. Chem.*, 1903, 38, 46—48).—It is well known that the administration of acid lessens the alkalinity of the blood. In the present research, it was found that alkaline substances (ammonia, trimethylamine) given to rabbits by inhalation increase it.

W. D. H.

Glycuronic Acid in the Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1903, 136, 1037—1039. Compare Abstr., 1901, ii, 610).—The glycuronic acid of dogs' blood exists exclusively in the corpuscles; none is found in the plasma. In whipped blood, however, some occurs in the serum.

After a meat diet, more glycuronic acid is found in the blood of the right ventricle than in that drawn from the carotid.

W. D. H.

Influence of Formaldehyde on Coagulation and Laking of Blood. CHARLES CLAUDE GUTHRIE (*Amer. J. Physiol.*, 1903, 9, 187—197).—Formaldehyde in quite small amounts hinders the process of blood-clotting. Some details as to its influence in the laking of blood by various reagents are also given.

W. D. H.

Destruction of Blood Corpuscles in Liver and Spleen. W. BAIN (*J. Physiol.*, 1903, 29, 352—368).—The surviving liver and spleen retain their power of destroying both red and white blood corpuscles. The action of the liver is mainly on the red corpuscles,

the corpuscles deficient in hæmoglobin being most affected. Most of the liberated hæmoglobin is retained by the liver and further destroyed, since the loosely-combined iron of the liver increases after perfusion, and the liver secretes much bile rich in pigment during the experiment. The main action of the spleen is on the leucocytes, especially those of the poly-morpho-nuclear kind, but a certain number of red ones are destroyed also. Free hæmoglobin is found in the serum of the defibrinated blood used.

W. D. H.

The Sugar in the Blood after Liver Ablation. FREDERICK W. PAVY and RAYMOND L. SIAU (*J. Physiol.*, 1903, 29, 375—381).—The statement of Bock and Hoffmann that on shutting off the liver from the circulation the sugar decreases and disappears from the blood in 45 minutes is at variance with later observations, including those described in the present paper. There is much variation in the rate of diminution, but the minimum (about 0.5 per cent.) is reached after the lapse of some hours. The quantity of sugar lost is, from the point of view of energy, insignificant. The experiments were made on cats.

W. D. H.

Fat-splitting Ferment of Gastric Juice. FRANZ VOLHARD (*Bied. Centr.*, 1903, 32, 394—395; from *Zeit. Klin. Med.*, 43, 397. Compare Abstr., 1901, ii, 518).—The ferment is very sensitive towards alkali, but resists the action of hydrogen chloride much more than the ferment of the mucous membrane extract. The activity of the ferment does not increase regularly, but at irregular intervals. Schütz and Boressow's law relating to the ferments of the digestive canal probably holds good in the case of the fat-splitting ferment.

N. H. J. M.

Reversibility of Lipolytic Action. HENRI POTTEVIN (*Compt., rend.*, 1903, 136, 1152—1155).—A glycerol extract of pancreas was employed in such excess that the quantities of glycerol and water produced or absorbed by ferment action did not modify its composition in any marked manner. If to this is added oleic acid, it is partially etherified, and if mono-olein is added, it undergoes partial splitting. In both cases, a condition of equilibrium is reached in which the same relative value obtains for free and combined acid. The value of this relation varies, other things being equal, with the amount of water in the pancreatic extract, rising with increase in the amount of water. When in any experiment the state of equilibrium is reached, the relation can be made to vary in one direction or the other according as water is added or removed from the mixture.

W. D. H.

Absorption and Fermentative Splitting of Disaccharides in the Small Intestine of Dogs. FRANZ RÜHMANN and J. NAGANO (*Pflüger's Archiv*, 1903, 95, 533—605).—The experiments were made on fully-grown dogs with a Vella's fistula. The rapidity of absorption is greatest for sucrose; maltose is more slowly, and lactose still more slowly, absorbed. Absorption occurs most rapidly in the upper part

of the intestine. The simpler sugars derived from disaccharides are more rapidly absorbed. Within certain limits, absorption increases with the concentration of the solution. The secretion of intestinal juice is not much affected by the concentration of the sugar solution. The relative weight of the mucous membrane is greater in the jejunum than in the ileum, more sugar being absorbed in the former situation. Water is most readily absorbed from solutions of the most readily absorbable sugars, but more rapidly from the ileum than from the jejunum. The juice from the jejunum contains very little invertin, and the action of this ferment on disaccharides is a feeble one; lactose is not affected at all. Inversion appears to be carried out by the cells of the mucous membrane, even in the ileum, where the juice secreted contains no invertin, but the action of the jejunal membrane is greater. If the concentration of the sucrose solution is greater than 5 per cent., some of the sugar passes into the circulation as such and is excreted by the kidneys. Lactose is but little affected by the mucous membrane in the upper part, and not at all in the lower portion of the intestine.

W. D. H.

Metabolism in Inanition. I. In Insects. B. SLOWTZOFF (*Beitr. chem. Physiol. Path.*, 1903, 4, 23—39).—The experiments made on the May fly show that in absolute inanition the animal loses about 24 per cent. of its weight. The daily loss is greatest at first, then falls to a minimum, rising, however, just before death. The loss is due to disappearance of water, fat, and proteid; chitin is unaffected. Of the proteids, those which are phosphorised are most affected. There is also a loss of inorganic salts, especially of those which are readily soluble. Full analytical figures are given.

W. D. H.

Intermediate Carbohydrate Metabolism. I. Ethylene Glycol and Glycolaldehyde. PAUL MAYER (*Zeit. physiol. Chem.*, 1903, 38, 135—156).—Experiments on rabbits show that ethylene glycol is oxidised in the body into glycollic acid and oxalic acid. About a quarter of the glycol administered leaves the body in the urine as glycollic acid. The freshly pounded liver is able to oxidise glycuronic into oxalic acid, but does not possess the same power in relation to glycol; this oxidation appears to occur in the kidney. After administration of glycolaldehyde, dextrose appears in the urine very rapidly; glycolaldehyde, glycollic acid, glyoxylic acid, and tetrose are absent. The sugar appears to be actually formed in the organism by condensation of the aldehyde.

W. D. H.

Degradation of Carbohydrates in the Animal Organism. A. BACH and F. BATTELLI (*Compt. rend.*, 1903, 136, 1351—1353).—It is suggested that the degradation of carbohydrates in the animal organism is brought about by the alternating action of two enzymes—the one, hydrolytic, and the other, oxidising in function (Stoklasa and Czerny this vol., ii, 321), carbon dioxide being a constant product of the activity of the former and water of the latter. It is assumed that

dextrose is first decomposed by the hydrolytic enzyme into lactic acid, then into alcohol and carbon dioxide. The alcohol is subsequently oxidised by the second enzyme, with the aid of the oxygen of the blood, to acetic acid, which, in turn, is decomposed into carbon dioxide and methane, the latter being finally oxidised to formic acid, from which, by the activity of the hydrolysing enzyme, carbon dioxide and hydrogen are produced, the latter being ultimately oxidised to water. The sum of the heats evolved in these reactions is equal to the heat of combustion of dextrose. The view adopted by Gautier and by Stoklasa (this vol., ii, 320, and 388), that energy is liberated by the anaërobic fermentation of carbohydrates, is not in harmony with known thermochemical facts.

T. A. H.

Behaviour of Stereoisomerides in the Animal System. II. The Transformations of the Three Mannoses in Rabbits. CARL NEUBERG and PAUL MAYER (*Zeit. physiol. Chem.*, 1903, 37, 530—544. Compare Neuberg and Wohlgemuth, *Abstr.*, 1902, ii, 336).—*d*-, *l*-, and *i*-Mannoses have been administered to rabbits per os, and by subcutaneous and by intravenous injection. In most cases, especially per os, *d*-mannose is completely used up, a very small part of the *l*-mannose is eliminated as such, and a further quantity as *l*-glucose; with *i*-mannose, a mixture of *l*- and *i*-mannoses and of *l*- and *i*-glucoses is obtained. With subcutaneous and intravenous injections, a portion of the *d*-mannose is eliminated as such.

l- and *i*-Mannoses can serve as a source of glycogen when the animal has been sufficiently deprived of food; in fact, the whole of the sugar may be used for this purpose.

J. J. S.

Production of Homogentisic Acid from Phenylalanine. W. FALTA and LEO LANGSTEIN (*Zeit. physiol. Chem.*, 1903, 37, 513—517).—Relatively large amounts of homogentisic acid, $C_6H_4(OH)_2 \cdot CO_2H$, are found in the urine of patients to whom phenylalanine (10 portions of 0.5 gram each in one day) has been administered. Practically 90 per cent. of the *l*-phenylalanine administered can be obtained in the form of excess of homogentisic acid. With *d*-*l*-phenylalanine, only some 50 per cent. is recovered in this form.

J. J. S.

Physiological Decomposition of Iodoalbumin. MAX MOSSE and CARL NEUBERG (*Zeit. physiol. Chem.*, 1903, 37, 427—441).—The earliest experiments of Hofmeister (*Abstr.*, 1898, i, 390) and Oswald (1899, ii, 439) have proved that the iodine of iodoproteids is eliminated as soluble metallic iodides in the urine of animals which have received only a relatively small amount of the iodine compound. The authors' experiments have been made on dogs and rabbits, and in each case the iodoalbumin was given on from 9—25 consecutive days, and after the lapse of several days the animal was killed and its various tissues examined. The iodoalbumin employed was a specimen of commercial sodium "iodeigon," consisting of the sodium salt of an iodated ovalbumin. In most of the tissues and animal liquids, soluble organic compounds containing iodine have been detected, and in the

liver and muscles of the rabbits insoluble iodinated proteids have also been recognised.

o-Iodolhippuric acid has been isolated from the urine of rabbits fed with the iodoalbumin, and *o*-iodobenzoic acid from the blood of dogs treated in the same manner. No definite compounds could be isolated from dogs' urine. The two compounds mentioned are not formed when the original iodoalbumin is boiled with hydrochloric acid. It is considered highly probable that the *o*-iodobenzoic and hippuric acids are obtained by the elimination of one or more substituents from more complex products.

J. J. S.

Inhibition of Precipitin Reactions. LEONOR MICHAELIS (*Beitr. chem. Physiol. Path.*, 1903, 4, 59—78).—The influences which inhibit precipitin reactions are partly general, partly specific. Solutions of all proteids, if sufficiently concentrated, will hinder, retard, or prevent the reaction. This is a general reaction. The addition of precipitin, previously heated to 72°, inhibits the reaction of fresh precipitin; this is specific, the inhibition being observed only if the same precipitin is used in both cases. An excess of precipitable substance hinders the precipitating action, and if a precipitate forms this dissolves on adding more precipitable substance.

W. D. H.

Kinase, Antikinase, and Protrypsin. A. DASTRE and A. STASSANO (*Compt. rend. Soc. Biol.*, 1903, 55, 633—635, 635—637).—The effect of antikinase on kinase is the result of inhibition, not destruction, of the latter ferment. Antikinase is destroyed spontaneously, especially at 37°; kinase is destroyed more slowly. When kinase is mixed with inactive pancreatic juice, it forms a powerful proteolytic mixture; kinase, however, preserves its individuality, as can be proved by the inhibiting effect which antikinase can still exert upon it.

W. D. H.

Photo-electric Changes in the Frog's Eye. FRANCIS GOTCH (*J. Physiol.*, 1903, 29, 388—410).—The photo-electric changes were studied with the capillary electrometer. Attention is drawn to the long latent period and sustained character of the response. The effects are monophasic, whether produced by illumination or shutting off the light. There are probably two chemical substances in the retina, one of which reacts to light, the other to darkness. For either change to occur markedly, the eye must be previously adapted, that is, the substance must undergo a phase of metabolism under conditions opposite to those which evoke the reaction. Thus, the favourable condition for obtaining a good effect on illumination is previous darkness, and the favourable condition for obtaining an effect on cessation of the light is previous illumination.

W. D. H.

Influence of Radium on the Growth of Animal Tissues. GEORGES BOHN (*Compt. rend.*, 1903, 136, 1012—1013).—The rays emitted from radium lessen the growth of animal tissues, as seen in experiments on various embryos. In epithelial tissues, the nucleus is

dislocated and pigment is produced. The rays appear to act on the chromatin of the cells. W. D. H.

Action of Calcium on the Heart. O. LANGENDORFF and WERNER HUECK (*Pflüger's Archiv*, 1903, 96, 473—485).—A number of experiments described on the hearts of both warm- and cold-blooded animals emphasise the importance of the action of calcium on the heart, and suggest its therapeutic use. W. D. H.

Action of Iodine on Lymphoid Tissues. MARCEL LABBÉ and LÉON LORTAT-JACOB (*Compt. rend. Soc. Biol.*, 1903, 55, 551—552).—In the guinea-pig, rabbit, and dog, iodine produces mono-nucleosis and is an excitant of the functions of lymphoid tissue. This coincides with its value in therapeutics. W. D. H.

Hæmolysis in the Spleen. DIARMID NOEL PATON and ALEXANDER GOODALL (*J. Physiol.*, 1903, 29, 411—439).—Removal of the spleen is not followed by any increase in any kind of blood corpuscles. The excess of red corpuscles added to the blood by injecting the blood of other animals disappears at the same rate whether the spleen is present or absent. Injection of water (a solvent of hæmoglobin) leads to exactly the same hæmolysis and recovery in normal and spleenless animals. Injection of agents toxic to the red corpuscles (such as tolylenediamine or phenylhydrazine) causes a great destruction of red and white corpuscles, but the anæmia, which resembles pernicious anæmia in many points, passes off in rabbits and dogs in about three weeks; pigment which gives the reactions of "free iron" occurs in the spleen, lymph glands, bone marrow, kidney, liver, and suprarenal cortex, in the order named. Regeneration is confined to the marrow, and the blood temporarily reverts to a foetal type. In spleenless animals, the anæmia is rather less about the fourth day because of the less rapid removal of dead red corpuscles from the circulation.

The anæmia induced by feeding rabbits on a diet poor in iron and proteid (rice) is more marked in spleenless than in normal animals, the spleen apparently acting as a storehouse for iron which would otherwise be lost.

There is no evidence that the spleen has any active hæmolytic power. It is rather a scavenger of the blood, removing dead red corpuscles, breaking down the hæmoglobin, and retaining the iron for use in the regeneration of the blood corpuscles. W. D. H.

Effects of Constituents of Ringer's Fluid on Skeletal Muscles. R. ROW (*J. Physiol.*, 1903, 29, 440—450).—Ringer's fluid and normal salt solution, when circulating through a skeletal muscle of *Rana hexadactyla*, behave exactly as they do on the heart, sodium chloride alone causing a gradual diminution of contractility and œdema. This takes only a few minutes. The calcium salt is responsible for the manifestation of contractions. If calcium is present, potassium salts produce no marked alteration. In toxic doses, potassium and calcium salts are antagonistic. W. D. H.

The Normal Presence of Lead in the Organism. G. MEILLÈRE (*Compt. rend. Soc. Biol.*, 1903, 55, 517—518, 518—520).—It is stated that the tissues, especially liver and spleen, contain traces of lead in nearly all the normal subjects examined. No doubt the impregnation is due to preserves, water, &c. It is remarkable how the quantity of lead may vary in many people without producing bad effects; this is attributed to idiosyncrasy or immunity, natural or acquired. The second paper relates to the distribution of lead in cases of plumbism. Most is found in bone, teeth, and brain; the liver and grey matter of the brain come next; then the kidneys; most of the other organs contain small amounts. Analytical figures are given. W. D. H.

Arsenic in Hens' Eggs. GABRIEL BERTRAND (*Compt. rend.*, 1903, 136, 1083—1085).—As a support to the doctrine that arsenic is a physiological constituent of living organisms, it is shown to occur in hens' eggs. A single egg contains about one two-hundredth of a milligram; most of this is in the yolk. W. D. H.

The Mesenteric Fat of *Thalassochelys Corticata* and *Cyprinus Carpio*. EMIL ZDAREK (*Zeit. physiol. Chem.*, 1903, 37, 460—463).—The oil from *Thalassochelys corticata* has a dark yellow colour and a disagreeable odour. It does not dissolve in 70 per cent. alcohol, and at the ordinary temperature is partly solid and partly liquid. The oil from *Cyprinus carpio* is very similar, but has a less objectionable odour. The following data are given:

	<i>Thalassochelys. Cyprinus.</i>	
Sp. gr. at 42.5°.....	0.9098	0.9107
Melting point	23—27°	25.6°
Solidifying point.....	10°	8.8°
Acid number	0.57	0.18
Saponification number	209	202.3
Mean mol. wt. of the fatty acids	268	277.7
Reichert-Meissl number.....	4.6	2.1
Iodine number.....	112	84.3
Iodine number of the fatty acids	119	84.2
Solidifying point of the fatty acids	28.2°	28.0°
Melting point of the fatty acids	30.2°	33.4°
Acetyl number	8.7	12.9
Acetyl number for the acids	203	201.1

J. J. S.

Glycogen. EDUARD PFLÜGER (*Pflüger's Archiv*, 1903, 96, 1—398).—A collation of facts in reference to glycogen, presenting mainly the author's work on the subject. W. D. H.

Meat Extracts. I. FRIEDRICH KUTSCHER and H. STEUDEL (*Zeit. physiol. Chem.*, 1903, 38, 101).—The main question investigated is the presence of succinic acid in meat extracts. Some authors regard this material as a product of putrefaction or autolysis, and some consider that it originates from phosphocarnic acid. Whether its absence is a

guarantee that the material from which the extract was prepared is blameless is a matter of doubt. The present paper does little more than raise these questions, but a further communication on the subject is promised. W. D. H.

Constitution of Snake Venom and Snake Sera. SIMON FLEXNER and HIDEYO NOGUCHI (*J. Pathol.*, 1903, 8, 379—410).—An account of numerous experiments on snake-poison and snake sera; the *Crotalus* was mainly investigated, and the research follows the lines of the usual routine on questions of immunity. W. D. H.

Chemistry of Sputum. FR. WANNER (*Chem. Centr.*, 1903, i, 985—986; from *Deutsch. Arch. klin. Med.*, '75, 347—377).—Sputum never contains true peptone; primary proteoses were also absent, but deutero-proteose is present; proteid decomposition in sputum is thus allied to what occurs on tryptic digestion. Albumin and globulin are present. Mucin was estimated by the amount of reducing substance formed after boiling with 10 per cent. hydrochloric acid. After antolysis of muco-purulent sputum, the cells are dissolved. Nucleo-proteid is formed, but the main proteid is proteose; true peptone was absent. Amino-acids are also formed. W. D. H.

Urobilin in Cows' Milk. A. DESMOULIÈRE and E. GAUTRELET (*Compt. rend. Soc. Biol.*, 1903, 55, 632—633).—In continuation of work which has shown urobilin to be present in blood and serous fluid, it is now stated that the yellow pigment of cows' milk usually described as a lipochrome, is wholly or almost entirely urobilin. W. D. H.

Diminution of the Lecithins in Milks Subjected to Heating. FRÉD. BORDAS and SIG. DE RACZOWSKI (*Ann. Chim. anal.*, 1903, 8, 168—169. Compare Abstr., 1902, ii, 587).—Experiments showing that milk may lose from 14 to 28 per cent. of its lecithin when heated over the naked fire at temperatures varying from 60° to 95°. When heated in an autoclave at 105—110°, the loss may amount to 30 per cent. The loss is reduced to about 12 per cent. when the milk is heated for 30 minutes at 95° on the water-bath. L. DE K.

Introduction of Foreign Bodies into the Gall-bladder. E. SCOTT CARMICHAEL (*J. Pathol.*, 1903, 8, 453—457).—Foreign bodies introduced into the gall-bladder of dogs and rabbits bring about the deposition of calculus-forming substances. The substance deposited is mainly calcium carbonate mixed with proteid, leucocytes, and desquamated epithelial cells. No cholesterol was found. These changes occur whether micro-organisms are present or not. W. D. H.

Formation of Gall-stones. VAUGHAN HARLEY and J. O. WAKELIN BARRATT (*J. Physiol.*, 1903, 29, 341—351).—If gall-stones are placed into the healthy gall-bladder of a dog, they disappear in from 6 to 12 months; bacteria are absent. If cholecystitis is present, the gall-stones introduced are not altered. In some of these cases, micro-organisms were present, in others absent. W. D. H.

Diuresis. VII. WILHELM FILEHNE and W. RUSCHHAUPT. VIII. WILHELM FILEHNE and H. BIBERFELD (*Pflüger's Archiv*, 1903, 95, 409—438, 439—446. Compare this vol., ii, 33).—Further researches on the influence of saline diuretics on the flow of urine which tell against the theories of filtration and reabsorption of the secretion. The first paper treats of the question in those cases where there is hindrance to the flow of water. The second treats mainly of the ability of the muscles to take up water under the influence of various drugs.

W. D. H.

Excretion of Glycuronic Acid. PAUL MAYER (*Chem. Centr.*, 1903, i, 1151—1152; from *Berlin klin. Woch.*, 40, 292—297. Compare Abstr., 1902, ii, 616).—Further experiments on this question are given, and the results of other authors, especially of Bial, are criticised. The author does not consider that Bial's methods prove the existence of glycuronic acid in the faeces.

W. D. H.

Phloridzin Glycosuria. FREDERICK W. PAVY, T. GREGOR BRODIE, and RAYMOND L. SIAU (*J. Physiol.*, 1903, 29, 467—491).—Injection of phloridzin into one renal artery produces glycosuria in that kidney prior to, and to a greater extent than from, the other. Perfusion of a surviving kidney with blood containing phloridzin produces diuresis and glycosuria; the amount of sugar in the urine cannot be accounted for by that which disappears from the blood. Intravenous injection of phloridzin after ablation of all the abdominal organs except the kidneys, produces glycosuria, and this persists after the blood-sugar has fallen to its lowest level. The effect is attributed to a specific action on the renal cells by which they acquire the power of producing sugar, probably from some constituent brought to them by the blood; what this constituent is, is unknown. The action may be compared to that by which lactose is set free by the cells of the mammary gland.

W. D. H.

Leucocytic Changes following Splenectomy combined with Intravenous Injections of Sodium Cinnamate. H. BATTY SHAW (*J. Pathol.*, 1903, 8, 435—442).—The experiments recorded, which were made on cats, confirm the view that the more complex leucocytes are derived from the simpler ones. Removal of the spleen combined with injections of sodium cinnamate intensifies the final conversion of intermediate cells into poly-morpho-nuclear cells, but injection alone will produce the same result.

W. D. H.

Proteid Precipitable by Acetic Acid in Pathological Urines. MATSUMOTO (*Chem. Centr.*, 1903, i, 986; from *Deutsch. Arch. klin. Med.*, 75, 398—411).—The greater part of the proteid precipitable by acetic acid from certain cases of pathological urine consists of fibrinoglobulin and euglobulin, and occasionally nucleoproteid in small amounts. Similar results were obtained with the pleural and peritoneal fluids.

W. D. H.

Action of Arsenic on the Bone Marrow of Man and Animals. RALPH STOCKMAN and FRANCIS J. CHARTERIS (*J. Pathol.*, 1903, 8, 443—447).—In small repeated doses, arsenic causes an increase in the

leucoblastic cells of the red marrow, little or no change in the erythroblastic cells, marked hyperæmia, and atrophy of fat-cells. No increase in the red corpuscles or hæmoglobin of the blood occurs. In larger doses which cause emaciation, the marrow undergoes hyaline degeneration, and the red corpuscles and hæmoglobin of the blood are diminished. Other poisons, however, produce similar effects. The beneficial action of arsenic in certain forms of intense anæmia is not due to any direct action on blood formation; the drug probably acts on the parasites to which such conditions are due.

W. D. H.

Physiological Action of Cæsium Chloride. G. A. HANFORD (*Amer. J. Physiol.*, 1903, 9, 214—237).—Cæsium chloride destroys the irritability of both muscle and nerve and in frogs produces paralysis. In mammals, death is caused by cardiac failure, and in addition to paralysis marked gastro-intestinal troubles occur. Its elimination by urine and fæces is rapid. No noteworthy effects on metabolism were observed. It produces no effect on cilia or red blood corpuscles.

W. D. H.

Physiological Action of Somnoform and Ethyl Bromide. SYDNEY W. COLE (*Proc. Physiol. Soc.*, 1903, xxv—xxvi; *J. Physiol.*, 29).—Somnoform is a mixture of ethyl chloride 65 parts, methyl chloride 30 parts, and ethyl bromide 5 parts. It has been introduced as an anæsthetic for minor operations. Its actions tested on animals differ from those of ethyl bromide in degree only. It increases the rate and tone of the diaphragm; in toxic doses, it causes death by tonic stoppage of this muscle, while the heart still beats strongly. This occurs after section of the vagi and is therefore an effect on the respiratory centre. Small doses cause a small rise of arterial pressure due to cardiac acceleration. With large doses, especially if the vagi are cut, the arterial pressure gradually falls and the heart is slowed. During the anæsthesia, vagus stimulation fails to affect the heart. This is due to the action of the anæsthetic on the ganglion cells in the heart or the preganglionic terminations around them. Muscular relaxation is seldom complete except with dangerous doses.

W. D. H.

Physiological Action of Phenanthrene Derivatives. P. BERGELL and ROBERT PSCHORR (*Zeit. physiol. Chem.*, 1903, 38, 16—38).—Phenanthrene is completely innocuous to the animal organism, and in rabbits is excreted as a compound with glycuronic acid. 2-, 3-, and 9-Hydroxyphenanthrenes produce tetanic convulsions; this is not affected by the position of the hydroxyl group. Phenanthrene-9-carboxylic acid and phenanthrene-3-sulphonic acid produce the same effect; the introduction of a methoxyl group (4-methoxyphenanthrene-9-carboxylic acid) influences this very little, but further introductions of alkyl and acyl groups (for example, 3-acetoxy-4:8-dimethoxyphenanthrene-9-carboxylic acid) lessen the toxicity. No narcotic action was observed. Whether the convulsive effects of morphine are due to the phenanthrene groups is still uncertain. Phenanthraquinone-3-sulphonic acid produces no tetanic effects, but both *in vivo*

and *in vitro* causes the formation of methæmoglobin; this is attributable to the quinone group.
W. D. H.

Antitoxic Effects of Urea and Sugars. EDMOND LESNÉ and CHARLES RICHER, jun. (*Compt. rend. Soc. Biol.*, 1903, 55, 590—592).—It is held that the toxicity of a poison can be raised or lowered by increasing or diminishing the proportion of non-toxic soluble substances. Thus intravenous injection of sodium chloride in the dog increases the amount of potassium iodide, ammonium salts, and cocaine required to cause death. It is now shown that other diffusible and inoffensive substances (urea and sugars) have the same effect, although to a less marked degree.
W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Decomposition of Cellulose by Aërobic Micro-organisms. G. VAN ITERSOM, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 5, 685—703).—The decomposition of cellulose by denitrifying bacteria has been studied. The experiments were carried out with Swedish filter paper. The cellulose is broken down by the action of denitrifying, non-spore forming, aërobic bacteria, provided that there is a limited supply of air. If nitrates be present in the nutritive medium, only nitrogen and carbon dioxide are evolved during the decomposition. Cellulose seems to exert no retarding influence on the nitrification of ammonium salts provided that there is a sufficient aëration. In the self-purification of waters and of the soil, and in the biological treatment of sewage, the combined actions of nitrification and denitrification play an important part in causing the disappearance of the cellulose.

Amongst the aërobic, non-spore forming bacteria which attack cellulose, the brown pigment bacterium, *Bacillus ferrugineus*, is predominant.

In nutrient media in which cellulose is being destroyed by aërobic bacteria after inoculation with ditch mud or garden soil, rich spirillæ cultures are obtained, and probably the distribution of spirillæ in nature is governed by cellulose. A chief cause of the brown colour of humus is a pigment formed from cellulose by bacteria or moulds. Most moulds attack cellulose, and the action is due to a specific enzyme for which the author suggests the name *cellulase*. The aërobic destruction of cellulose accounts for the fact that wood or rope partly immersed in water become weak at the place of contact of water and air.
J. McC.

A Mould Converting Quinic Acid into Protocatechuic Acid. OSKAR EMMERLING and EMIL ABDERHALDEN (*Centr. Bakt. Par.*, 1903, 10, 337—339).—The conversion by moulds, of quinic acid into proto-

catechuic acid, previously observed by Löw (Abstr., 1881, 602), is found to be caused, to the extent of 12 per cent., by a mould, *Micrococcus chinicus*, isolated from putrid meat extract. The change does not occur to any considerable extent in the absence of air.

Ten per cent. solutions of sodium citrate are partially converted by putrid meat extract into acetic and succinic acids, this being due, however, not to *M. chinicus*, but to other moulds which are still under examination.

G. D. L.

Composition of the Tubercle Bacilli derived from various Animals. E. A. DE SCHWEINITZ and M. DORSET (*J. Amer. Chem. Soc.*, 1903, 25, 354—358).—The following amounts of ether, alcohol, and chloroform extracts were found in (1) bovine, (2) swine, (3) horse, (4) avian, (5 and 6) attenuated and virulent human tubercle bacilli after washing out any adherent culture-media and most of the constituents soluble in water :

	1.	2.	3.	4.	5.	6.
Ether extract	17.70	12.56	23.38	17.36	28.72	20.31
Alcohol extract.....	8.13	7.83	8.18	13.27	7.36	7.22
Chloroform extract ...	0.49	0.20	0.20	0.02	1.33	0.48

The acid values of the ether and alcohol extracts, the total ash, and the phosphoric acid were also determined.

It is suggested that the virulent human, bovine, horse, and swine tubercle bacilli, which contain less harmless matter than the attenuated human tubercle bacilli, produce greater amounts of poisonous proteids.

It was previously shown (*Centr. Bakt. Par.*, 1897, 22, i, 209) that cultivations of human tubercle bacilli contain a very virulent acid-like necrotic substance. This, being readily soluble in water, would not be included in the above extracts.

N. H. J. M.

Fat of Tubercle Bacilli. KARL J. KRESLING (*Chem. Centr.*, 1903, i, 1153; from *Arch. Soc. biol. St. Petersb.*, 9, 359—376).—The dry substance obtained from tubercle bacilli in the preparation of tuberculin contained 3.94 per cent. of water, 8.57 of nitrogen, 38.95 of fat, and 0.97 of other organic substances not containing nitrogen. The percentage of nitrogen corresponds with 53.59 of proteid substances, if the nitrogen contained in the lecithins and other compounds which are soluble in chloroform, benzene, ether, and alcohol is neglected. The fatty substances extracted by chloroform melt at 46°, have an acid number 23.08, Reichert-Meissl number 2.01, Hühner number 74.23, saponification number 60.70, ester number 37.62, and Hübl iodine number 9.92. They contain 14.38 per cent. of free fatty acids, 77.25 of neutral fats or esters, 39.10 of alcohols extracted from the esters and melting at 43.5—44°, 0.16 of lecithin, and 7.3 of substances soluble in water; 25.76 per cent. of substances soluble in water are extracted after the complete hydrolysis of the fats.

E. W. W.

Biology of Yeast. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1903, 37, 396—399).—Different substances have been introduced into yeast which has been allowed to undergo spontaneous fermentation.

Usually 10 grams of the substance were left for 2—3 weeks in contact with 2 litres of well-washed yeast at a temperature of 38°, toluene being added if necessary.

It has been found that salicyl alcohol is oxidised to the corresponding acid; thymol is oxidised to an *acid* melting at 187°, and cymene yields crystals of a compound containing nitrogen.

The numbers obtained by Hansen for the time required for spore development of different species of *Saccharomyces* at different temperatures have been employed for the calculation of the velocity of spore formation and velocity-temperature curves have been constructed using these values. The curves are of the usual form, and each shows a maximum (compare Tammann, *Abstr.*, 1892, 899). J. J. S.

Assimilation of Carbon Dioxide in Green Plants. THOMAS BOKORNY (*Chem. Zeit.*, 1903, 27, 525—527. Compare *Abstr.*, 1902, ii, 345).—Experiments with *Petroselinum sativum* showed that assimilation is checked in solutions containing 1 part of formaldehyde in 20,000, and even by 1 in 50,000. It is therefore impossible for appreciable amounts of formaldehyde to accumulate in plants. There is nothing improbable in the assumption that formaldehyde is immediately converted into carbohydrate. As regards the assumed reduction of carbon monoxide, however, it is pointed out that production of hydrogen has hitherto only been observed in fermentation processes. The conclusion is drawn that hydrogen carbonate is directly reduced to formaldehyde by the chlorophyll-apparatus in presence of an adequate amount of light. N. H. J. M.

Rôle of Calcium Oxalate in Plant Nutrition. AMAR (*Compt. rend.*, 1903, 136, 901—902).—Several caryophyllous plants, with five or six pairs of leaves, were removed from the soil and transferred to nutritive solutions free from calcium. On examining the leaves 55 days afterwards, it was found that the recently developed upper leaves did not contain calcium oxalate, whilst the lower leaves were normal in this respect. The same applies to the stems. Similar plants germinated and grown in the same nutritive solution were quite free from calcium oxalate. N. H. J. M.

Influence of Formaldehyde on the Vegetation of White Mustard. RAOUL BOUILHAC and ERCOLE GIUSTINIANI (*Compt. rend.*, 1903, 136, 1155—1157).—White mustard was successfully grown in mineral solutions containing formaldehyde when the amount of light was insufficient for normal chlorophyllous assimilation. When, however, the amount of light was further diminished, the plants died. A certain quantity of light seems to be necessary for the assimilation of formaldehyde. N. H. J. M.

Influence of the Nature of External Media on Vegetable Acidity. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1903, 136, 1009—1011).—When peppermint plants were manured with mineral salts, there was in every case an increase of volatile acids in

the fresh leaves. The amounts of volatile acids in the dry leaves were more irregular; it was found that chlorides and sulphates slightly increase and that nitrates seem to decrease the volatile acids in the fresh leaves. With disodium hydrogen phosphate, there was a marked increase in the volatile acids.

The same groups of salts which cause the greatest diminution in the amount of water in plants (this vol., ii, 233) give rise to the highest ratio between the volatile acids present as esters and the total volatile acids.

As regards the alkalinity of the ash, it was found that, at the beginning of the vegetative period, the ash of the growth above ground was more alkaline than that of the roots. As the plants develop, alkalinity decreases in the above-ground portions and increases in the roots, so that finally the ash of the roots is more alkaline than that of the above-ground portions of the plant.

The general effect of mineral salts is to increase the amount of combined acids in the parts of the plants above ground; the differences are not very appreciable in the roots. N. H. J. M.

Some Proteolytic Ferments Associated with Rennet in Plants. MAURICE JAVILLIER (*Compt. rend.*, 1903, 136, 1013—1015. Compare Abstr., 1902, ii, 625).—The sap of *Lolium* and other plants was found to contain casease and gelatinase, two allied diastases which may be identical. *Lolium* also contains a diastase which, like Cohnheim's erepsin, acts on peptone. Lucerne contains neither casease nor erepsin.

Casease and erepsin seem to be frequently associated, and it is suggested that they are possibly identical. N. H. J. M.

Synthesis of Proteids by Plants. ÉMILE LAURENT and ÉM. MARCHAL (*Bull. Acad. roy. Belg.*, 1903, 55—114).—Nitrogen in the form of ammonia is assimilated both by normal and by etiolated chlorophyllous plants, assimilation being more active in normal plants. Assimilation of nitrogen in the form of nitrates by green plants is, with some exceptions, far more intense in presence of light than in darkness. When nitrogen (elementary nitrogen and nitrogen as ammonia or as nitrates) is assimilated in absence of light, the necessary energy is supplied by the consumption of carbohydrates.

Whilst lower non-chlorophyllous plants are able to produce proteids in absence of light, the synthesis in higher chlorophyllous plants can only take place in presence of light. N. H. J. M.

Effect of Deficiency of Nitrogen, Phosphoric Acid, and Potassium on Plants. H. WILFARTH and G. WIMMER (*J. Landw.*, 1903, 51, 129—138. Compare Abstr., 1902, ii, 221).—When nitrogen or phosphoric acid is deficient, growth is more or less restricted, but the composition of the dry matter is only affected when the deficiency is very great. With insufficient amounts of phosphoric acid, the leaves acquire a dark green or bluish-green colour

according to the amount of nitrogen present, or, in extreme cases, the leaves blacken, first at the edges.

Very small amounts of potassium enable plants to grow and to maintain their normal appearance for weeks or months. When, however, the potassium is used up, assimilation of carbon dioxide ceases.

Sugar-beet grown without sufficient potassium readily decays, and the sugar is frequently converted, partially or entirely, into invert sugar. As in the case of sugar-beet, the proportion of leaves in potatoes is considerably increased when potassium is deficient; the yield and size of the tubers and the percentage of starch are reduced.

The effect of want of potassium on the appearance of the leaves of plants is frequently very difficult to distinguish from that of fungi and insects, and there is no doubt that the abnormal appearance of leaves is often attributed to the wrong cause. N. H. J. M.

Localisation of Æsculin and Tannin in Horse Chesnut. A. GORIS (*Compt. rend.*, 1903, 136, 902—904).—Æsculin is produced independently of sunlight, and is always accompanied by tannin. The substances are not utilised in the development of new organs.

N. H. J. M.

Digestibility of Pentosans. STEPHAN WEISER (*Landw. Versuchs-Stat.*, 1903, 58, 238—240).—The results of experiments with bullocks, pigs, sheep, and horses showed that the greater part of the pentosans (determined by the phloroglucinol method both in food and in fæces) was digested.

Further experiments showed that the digestibility of pentosans corresponds with that of the cellulose. The more crude fibre was digested, the greater was the digestibility coefficient of the pentosans.

N. H. J. M.

Molasses Food. MAX GONNERMANN (*Milch. Zeit.*, 1903, 32, 324—326. Compare Abstr., 1901, ii, 71).—Peat molasses remains for a long time unaltered, especially after addition of a little milk of lime. It should be mixed with an equal amount of oil-seed meal as required.

N. H. J. M.

Drying Sugar-beet Leaves. FRANZ LEHMANN and CREYDT (*Bied. Centr.*, 1903, 32, 398—403; from *Hannov. Land.-u. Forstwiss. Zeit.*, 55, 21, 22, 23).—A readily digestible food is obtained by drying sugar-beet leaves, provided that care is taken to avoid too high a temperature. It is unnecessary to get rid of the oxalic acid as it is destroyed by ferments in the stomachs of ruminants. The results of experiments with sheep showed that 3 parts of the dried leaves are equivalent to 2 of rye bran. Further experiments, in which two lots of bullocks were fattened with mixed foods containing respectively 10 lbs. of dried sugar-beet leaves and 6 lbs. of wheat husks, showed

that in a period of 4 months the bullocks fed with beet leaves gained 0.1 lb. per day more than those which had wheat husks.

The average composition of the dried leaves was as follows :

Proteids.	Fat.	Carbo- hydrates.	Crude fibre.	Pure ash.	Sand.	Water.
9.66	1.16	40.34	8.70	8.80	18.65	12.69.

The carbohydrates include 15—16 per cent. of sugar.

The drying process employed is similar to that used for the roots and must be continuous.

It is preferable to feed the fresh roots when this is possible.

N. H. J. M.

Proteids and some other Nitrogen Compounds in Plants. N. NEDOKUTSCHIAËFF (*Landw. Versuchs-Stat.*, 1903, 58, 275—280. Compare Abstr., 1902, ii, 281).—The following amounts of nitrogen were found in wheat grain at five different periods :

	Total N.	Nitrogen as proteids.			Non-proteid nitrogen.			
		Insoluble.	Coagulable.	Albumoses.	1.	2.	3.	4.
June 18th	3.498	1.944	0.098	0.431	0.480	0.053	0.381	0.164
„ 25th	2.456	1.822	0.081	0.212	0.206	0.045	0.108	0.127
July 2nd	2.293	1.888	0.073	0.109	0.103	0.018	—	0.115
„ 9th	2.357	1.941	0.114	0.053	—	0.009	—	—
„ 21st	2.401	2.019	0.143	0.138	0.070	0.006	—	0.031

The numbers given under non-proteid nitrogen refer to (1) the phosphotungstic acid precipitates, (2) xanthine bases, (3) nitrogen separated by boiling with acid, and (4) undetermined.

Wheat grain contains soluble proteids which are only completely coagulated when heated under a pressure of $1\frac{1}{2}$ atmospheres. The albumoses were separated by means of zinc sulphate. The results obtained by this method (Laszczynski, *Zeit. ges. Brauwes.*, 1889, 22) are somewhat higher than those obtained by Stutzer's method, as albumoses are not completely separated by cupric hydroxide.

N. H. J. M.

Nitrogenous Compounds in Arable Soil. GUSTAVE ANDRÉ (*Compt. rend.*, 1903, 136, 820—822. Compare this vol., ii, 235).—The amount of ammonia found in April in surface soil and in samples from depths of 35 and 65 cm. greatly increased, in relation to the total nitrogen, with the depth, the percentage of ammonia in total nitrogen being 0.51, 1.08, and 5.15 respectively. By the following October, the percentages were similar in the three samples (0.49—0.44, 0.31—0.28, and 0.33—0.72 on October 25—27).

The losses of ammonia in drainage are very slight, and seem to be greatest in the spring.

N. H. J. M.

Atmospheric Precipitations. B. WELBEL (*Bied. Centr.*, 1903, 32, 291—293; from *Travaux Stat. expér. agron. Ploty.*, 1900, 44, and 1901, 42).—The rainfall of 1900 and 1901 amounted to 421.6 and

549.8 mm. respectively. The rain-water contained : ammonia, 1.091 and 1.068 ; nitrous acid, 0.058 and 0.021 ; and nitric acid, 0.023 and 0.280 per million. Nitrous acid was absent in the rain of June, July, August, and September, and the amount was very small in April, May, and October, but greater in December to March. The smallest amount of ammonia was found in snow, the greatest in dew.

The total nitrogen per annum was 3.9 kilograms per hectare in 1900, and 5.2 kilograms in 1902. N. H. J. M.

Lysimeter Water. B. WELBEL (*Bied. Centr.*, 1903, 32, 293—296 ; from *Travaux Stat. expér. agron. Ploty.*, 1900, 49).—The lysimeters had each an area of 500 cm. square, and were respectively (two of each) 30, 45, and 100 cm. deep. One of each depth was covered with turf in June and July, and in the spring of the next year oats were sown in the same lysimeters.

The most prominent constituents of the drainage were organic compounds, calcium compounds, and nitrates ; potassium and phosphoric acid were less abundant, and sulphuric acid was only found in traces.

The following amounts of nitric acid (grams per square metre) were found in the drainage of the two lysimeters (30 cm. and 45 cm. deep) without vegetation (1 and 2) and the two with vegetation (1a and 2a) :

	1.	2.	1a.	2a.
Nitric acid (grams) ...	10.70	19.07	7.04	3.93.

N. H. J. M.

Analytical Chemistry.

Titanium Trichloride in Volumetric Analysis. EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1903, 36, 1549—1555. Compare this vol., ii, 217).—A standard solution of titanium trichloride is prepared by diluting the commercial solution with twenty times its volume of water and titrating against a solution of a ferric salt of known strength, for example, one prepared by oxidising a weighed quantity of ferrous ammonium sulphate ; before dilution, it is advisable to boil the commercial salt with an equal volume of concentrated hydrochloric acid so as to expel traces of hydrogen sulphide. The solution is stored under a constant pressure of hydrogen in a 1—2 litre bottle connected by a tubulus with a refilling burette, and does not then alter in strength. It can be used for determining the strength of a ferric solution by adding it to the latter until a drop taken out gives no red coloration with a solution of a thiocyanate. To estimate both ferrous and ferric salts in a solution, the ferrous iron is oxidised with potassium permanganate and then the total ferric salt reduced with the titanium chloride.

The solution reduces azo-compounds quantitatively, and therefore

can be used for their analysis; azo-compounds which are insoluble in water are first sulphonated with fuming sulphuric acid and then titrated. Nitro-compounds also, for example, nitrobenzene, *p*-nitroaniline, and picric acid, are reduced quantitatively to the corresponding bases. Examples are given showing the degree of accuracy of the method.

W. A. D.

New Process for Estimating Halogens in Organic Compounds. HENRI BAUBIGNY and G. CHAVANNE (*Compt. rend.*, 1903, 136, 1197—1199).—By the ordinary processes, the halogens in organic substances cannot be separated, but when a compound containing halogens is oxidised with a chromic acid mixture, the chlorine and bromine are expelled and the iodine is oxidised to iodate. The mixture is prepared by adding 1 to 1.5 grams of silver nitrate to about 40 c.c. of sulphuric acid (sp. gr. 1.84) and warming until the salt is dissolved. Four to eight grams of potassium dichromate are then added and the mixture warmed until complete dissolution takes place. This mixture is slowly poured on to the weighed substance with constant agitation, and the temperature is gradually raised to 150—170°. To the cooled mixture, 140 to 150 c.c. of water are added, and the iodate is reduced by means of sulphurous acid. Crystals of silver chromate mixed with silver iodate are sometimes deposited along with the silver iodide; when this happens, they are dissolved in a solution of ammonium nitrate, and the iodate reduced as before. The silver iodide is frequently contaminated with silver sulphate, from which it can be freed by digesting with warm, dilute nitric acid. Results are given which show the accuracy of the method. The oxidation only requires about fifteen minutes.

J. McC.

Separation of Bromine and the Thiocyanate Radicle. FRIEDRICH W. KÜSTER and ALFRED THIEL (*Zeit. anorg. Chem.*, 1903, 35, 41—44).—The authors have already shown (this vol., ii, 136) how a bromide and thiocyanate may be estimated together by converting into the silver salts and heating in a current of chlorine. This process, like that suggested by Rupp and modified by Thiel (*Abstr.*, 1902, ii, 706), is slow, and a quicker method is now described.

A bromide can be quantitatively estimated by distilling with a chromic acid mixture into potassium iodide solution and determining the amount of iodine liberated. A thiocyanate similarly treated causes no separation of iodine, but if a bromide and a thiocyanate together be so treated too much iodine is liberated. This is attributed to the formation of cyanogen bromide, which exerts an oxidising action on the potassium iodide. In order to avoid this, the mixture is distilled with chromic acid and the distillate collected in dilute potassium hydroxide solution. To this solution is then added potassium permanganate solution and sulphuric acid, and it is distilled into potassium iodide solution until all the bromine is expelled. The method gives good results.

J. McC.

Source of Error when Testing for Iodine in Urines. MARCEL GUERBET (*J. Pharm. Chim.*, 1903, [vi], 17, 313—314).—The usual process is to ignite the dry residue from the urine in the presence of potassium hydroxide, and afterwards test the solution of the ash for iodine in the usual manner.

The author has noticed that traces of potassium cyanide are formed during the ignition, and these interfere with, or altogether prevent, the reactions for iodine. The cyanide should therefore be expelled by boiling the solution with a slight excess of sulphuric acid; the test for iodine will then be successful.

L. DE K.

The Citrate Method for the Estimation of Phosphoric Acid in Basic Slags. NORBERT VON LORENZ (*Chem. Zeit.*, 1903, 27, 495—496).—An adverse criticism of the "citrate process." The author calls attention to his method of weighing the ether-washed ammonium phosphomolybdate, which he thinks better than the process recommended by Woy (this vol., ii, 390).

L. DE K.

Estimation of Total Phosphoric Acid and Potassium in Soils. CHARLES B. WILLIAMS (*J. Amer. Chem. Soc.*, 1903, 25, 491—496).—The well-sampled soil is ignited and the ash treated three times with hydrofluoric acid. The dry residue is fused with potassium sodium carbonate, and from the fused mass the remaining silica is removed in the usual way by evaporation with hydrochloric acid. The mass is dissolved in dilute hydrochloric acid and the filtrate evaporated to a small bulk with addition of excess of nitric acid. The phosphoric acid is then estimated volumetrically by the author's molybdate process (*Abstr.*, 1901, ii, 344).

For the estimation of the potassium, the soil is evaporated with sulphuric acid, and after the excess of acid has been expelled, the residue is treated 5 times with hydrofluoric acid. After adding a little sulphuric acid, the mass is gently ignited until no more fumes are visible. The mass is then extracted with water and, after removing any iron, aluminium, calcium, &c., by means of ammonia and ammonium oxalate, the filtrate is treated in the usual way, finally by the Lindo-Gladding method.

L. DE K.

Estimation of Potassium in Fertilisers; Substitution of Calcium Hydroxide for Ammonia and Ammonium Oxalate. C. L. HARE (*J. Amer. Chem. Soc.*, 1903, 25, 416—420).—A method originally proposed by Ross. Ten grams of the sample are boiled with 350 c.c. of water, a slight excess of milk of lime is added, and when cold the whole is made up to 500 c.c. Fifty c.c. of the filtrate are acidified with hydrochloric acid and evaporated nearly to dryness with addition of platinic chloride. The residue is then washed, as usual, with alcohol and ammonium chloride solution (Lindo-Gladding method).

When the fertiliser contains organic matter, this is first got rid of by evaporating with dilute sulphuric acid and incinerating the residue. The small quantity of calcium sulphate which contaminates the

platinum precipitate is dissolved by the ammonium chloride solution. The author has also obtained good results by simply boiling with water without previous destruction of the organic matter.

L. DE K.

Estimation of Total Alkalis in Soils. J. H. PETTIT (*J. Amer. Chem. Soc.*, 1903, 26, 496—498).—Owing to the difficulty of completely separating the last traces of barium from the alkali chlorides by means of ammonium carbonate, the author uses a solution of ammonium sulphate. The filtrate is then evaporated to dryness, and on ignition the chlorides are completely converted into sulphates, which may then be weighed. Towards the end of the heating, a little ammonium carbonate should be thrown into the dish to destroy any acid sulphates.

L. DE K.

Detection of Lead and Manganese. AUGUSTE TRILLAT (*Compt. rend.*, 1903, 136, 1205—1207).—In acetic acid solution, tetramethyldiaminodiphenylmethane gives a deep blue colour with lead and manganese dioxides. This reaction is extremely delicate and may be used for the detection of these metals. The reagent is prepared by boiling 30 grams of dimethylaniline with 10 grams of formaldehyde and 200 c.c. of water. After cooling, the liquid is made alkaline with sodium hydroxide and a current of steam is blown through until the excess of dimethylaniline is expelled. On cooling, crystals separate which should be recrystallised from alcohol. Five grams of the base are dissolved in 100 c.c. of water and 10 c.c. of acetic acid; the solution must be placed in a well-stoppered bottle and preserved in the dark. To test for lead, the suspected substance is incinerated with sulphuric acid, and two drops of a saturated solution of sodium hypochlorite added for every 0.01 gram of ash. The chlorine is expelled by washing or by heating, and if lead is present a blue coloration is obtained on addition of the above reagent. In this way, lead has been detected in water which had passed through lead pipes, although it eluded detection by other methods. The method also showed the presence of lead in the stomach, blood, and urine of a rabbit which had absorbed 0.15 gram of lead acetate.

To test for manganese, the suspected substance is treated with sodium hydroxide, then incinerated. The ash is moistened with acetic acid, then, if manganese be present, a blue coloration is developed on warming with the reagent. By this means, manganese has been detected in various vegetables. Care should be taken that copper is absent, for this may give rise to a blue coloration.

J. McC.

[**Volumetric Estimation of Cerium.**] ANTON WAEGNER and A. MÜLLER (*Ber.*, 1903, 36, 1732. Compare this vol., ii, 242).—The use of bismuth tetroxide in testing for cerium was first suggested by Gibbs (*Amer. Chem. J.*, 1893, 15, 546).

T. M. L.

Precipitation of Manganese from Acid Solutions by Persulphuric Acid. HENRI BAUBIGNY (*Compt. rend.*, 1903, 136, 1325—1327. Compare this vol., ii, 184, 335).—The precipitation of

manganese as the peroxide by ammonium persulphate is practically independent of the volume of the solution so long as the persulphate is added in excess and the acidity of the liquid is not too great. The applicability of the method is limited by the last condition, since in presence of 5 per cent. of sulphuric acid complete precipitation occurs at 50° , whilst for 8 per cent. the temperature must be raised to $85-86^{\circ}$, and for 10 per cent. the necessary temperature is 100° . This is due to the rapidity with which persulphuric acid decomposes in hot dilute sulphuric acid.

T. A. H.

Volumetric Estimation of Manganese in Iron and Steel. HARRY E. WALTERS (*J. Amer. Chem. Soc.*, 1903, 25, 392—394).—A reply to Stehman (this vol., ii, 243). It is not necessary to remove the excess of silver nitrate, if the solution is allowed to get cold before titrating with either hydrogen peroxide or sodium arsenite.

L. DE K.

Electrolytic Separation (1) of Manganese and Iron, (2) of Aluminium and Iron or Nickel, and (3) of Zinc and Iron. AUGUSTE HOLLARD and BERTIAUX (*Compt. rend.*, 1903, 136, 1266—1268).—(1) Iron and manganese can be simultaneously deposited electrolytically, the iron at the cathode and the manganese as peroxide at the anode. The manganese peroxide is apt to carry some iron with it, but this can be avoided by the addition of sulphurous acid. The metals should be in the form of sulphates and the solution should contain ammonium citrate and ammonium sulphate. A platinum basin is used as cathode and a platinum spiral as anode. If the proper proportion of sulphurous acid has been added, the iron is completely deposited (1 ampere; temperature, 48°) before the manganese peroxide begins to form at the anode. The solution is removed, the iron dissolved in dilute sulphuric acid, and estimated by titration with potassium permanganate. The solution is replaced and the basin made the anode. The electrolysis is carried out with a current of 1 ampere at $90-95^{\circ}$. The deposited manganese peroxide is estimated by ascertaining how much iodine is liberated by it from an acid solution of potassium iodide.

(2) The addition of sulphurous acid is also advantageous in the separation of iron from aluminium electrolytically because it prevents the formation of aluminium hydroxide and also prevents the deposition of basic salts of iron.

(3) Zinc and iron can be separated electrolytically by first adding sulphurous acid to the solution of the sulphates, then, after nearly neutralising with sodium hydroxide, adding potassium cyanide, which produces potassium ferrocyanide, and from the solution only zinc is deposited.

J. McC.

Estimation of Antimony. LEWIS A. YOUTZ (*Zeit. anorg. Chem.* 1903, 35, 55—65).—Although the boiling points of arsenic chloride (134°), antimony trichloride (223°), and stannic chloride (114°) lie considerably apart, no separation of tin and antimony can be effected by distillation of a hydrochloric acid solution of these substances.

Various determinations of the temperature at which the chlorides volatilise from hydrochloric acid solutions have been made.

On account of the formation of antimonious acid, antimony is completely non-volatile at the boiling point of hydrochloric acid from a solution obtained by oxidising with nitric acid or potassium chlorate.

J. McC.

Assay of Platinum, and of its Alloys with the Precious Metals. EMILIEN NEVEU (*Ann. Chim. anal.*, 1903, 8, 161—164).—The alloy is, if necessary, melted with a known weight of pure gold so that this will exceed the platinum by about 4 to 1. The mass is then heated with sulphuric acid free from nitric compounds, and the undissolved matter is heated and reweighed, when the loss represents the bulk of the silver, &c. It is then fused with eight times its weight of pure cadmium and a little potassium cyanide, the mass is granulated by pouring it into water, and after the cyanide has dissolved, the metal is thoroughly washed and treated with nitric acid of sp. gr. 1.27, which extracts the remainder of the silver and leaves the gold and platinum undissolved; these are then separated as usual.

The silver is determined as usual by standard salt solution, but it is best to introduce into the liquid exactly 1 gram of metallic silver (which is then allowed for) or else a few grams of recently precipitated well-washed silver chloride in order to facilitate the operation.

L. DE K.

Estimation of Benzene in Illuminating Gas. LOUIS M. DENNIS and J. G. O'NEILL (*J. Amer. Chem. Soc.*, 1903, 26, 503—511).—Benzene may be quantitatively removed from coal gas by means of an ammoniacal solution of nickel nitrate prepared as follows: 40 grams of nickel nitrate are dissolved in 160 c.c. of water and 2 c.c. of nitric acid of sp. gr. 1.44. This solution is then poured slowly into 100 c.c. of ammonia of sp. gr. 0.908. The authors recommend the following procedure: carbon dioxide is removed by potassium hydroxide, the benzene is then absorbed by the nickel solution, heavy hydrocarbons are removed by fuming sulphuric acid, oxygen is absorbed by phosphorus or an alkaline solution of pyrogallol, carbon monoxide is removed by cuprous chloride, and the methane and hydrogen are determined as usual.

L. DE K.

New Reaction for Certain Alcohols and Allied Substances. GAVARD (*J. Pharm. Chim.*, 1903, [vi], 17, 374—375).—If a little ether is carefully poured over the surface of sulphuric acid containing 5—20 per cent. of potassium nitrite, a fine blue colour is developed. On warming or shaking, the colour disappears and nitrogen dioxide is evolved. After a time, the colour will return, and it may be made to disappear and reappear some ten times. A temperature of -20° also prevents the reaction. The following substances also give the reaction: trioxymethylene, formaldehyde, acetone, acetaldehyde, methyl, ethyl, amyl, propyl, isopropyl, butyl, and isobutyl alcohols, sorbitol, dulcitol, mannitol, erythritol, benzyl alcohol, formic acid, trichloroacetic

acid, lactic acid, ethyl acetate, amyl acetate, ethyl oxalate, acetal, levulose, dextrose, xylose, arabinose, raffinose, and sucrose.

When the substance is solid, a few particles are dropped on to the surface of the acid and immediately an equal bulk of water is added carefully.

L. DE K.

Estimation of Glycerol in Soap-lyes. RICHARD FANTO (*Zeit. angew. Chem.*, 1903, 16, 413—414).—The process previously described by Zeisel and Fanto (*Abstr.*, 1902, ii, 111, 585) is recommended for the estimation of glycerol in spent soap-lyes. In order to obtain accurate results, it is advisable to precipitate the chlorine with the calculated quantity of silver sulphate and the sulphates with solution of barium acetate. A quantity of the filtrate equal to 1 c.c. of the original sample is then treated with hydriodic acid as previously directed.

L. DE K.

New Process for the Estimation of Glycerol. A. BUISINE (*Compt. rend.*, 1903, 136, 1204—1205. Compare this vol., i, 456).—When glycerol is heated at 350° with potash-lime, reaction takes place according to the equation: $C_3H_8O_3 + 4KOH = 2K_2CO_3 + 3H_2 + CH_4 + H_2O$, and the estimation of the glycerol may be carried out by measuring the volume of gas produced. Two-tenths to half a gram of the glycerol is mixed with 4 to 5 grams of powdered potassium hydroxide and 15 to 20 grams of potash-lime, the mixture placed in a flask connected with a gas measuring vessel, and the flask heated in a mercury bath at 350°. The evolution of gas requires about an hour. One gram of glycerol gives 967 c.c. of gas at 0° and 760 mm. Results are given showing the accuracy of the method.

J. McC.

Estimation of Starch in Substances containing Pentosans. STEPHAN WEISER and ARTHUR ZAITSCHEK (*Landw. Versuchs-Stat.*, 1903, 58, 219—231. Compare this vol., ii, 225).—In estimating the starch in hay, the finely-powdered substance (5 grams) is first heated with water for 4 hours under a pressure of 3 atmospheres. The filtered solution, diluted to 200 c.c., is boiled for 3 hours with 20 c.c. of hydrochloric acid of sp. gr. 1.125, neutralised, and diluted to 500 c.c. The copper reducing power is then determined in 50 c.c. The amount of pentosans is next determined in 150 c.c. of the solution.

The following results show the method of calculating the amount of starch. The copper reducing power of 50 c.c. (= 0.5 gram of substance) was equivalent to 59.5 mg. of dextrose or 12.51 per cent. of starch in the dry matter. The 150 c.c. of solution contained 49.2 mg. of pentoses, or 16.4 mg. in 50 c.c., from which amount 0.4 mg. is deducted (the amount corresponding with the furfuraldehyde yielded by the dextrose). The 16 mg. of pentoses are then deducted from the 59.5 mg. of dextrose leaving 43.5 mg. of dextrose, corresponding with 9.16 per cent. of starch, instead of 12.51 per cent., the amount found if the pentoses are not taken into account.

Tables are given showing the copper reducing power of arabinose and xylose.

N. H. J. M.

Estimation of Carbohydrates in Fæces. STEPHAN WEISER and ARTHUR ZAITSCHEK (*Landw. Versuchs-Stat.*, 1903, 58, 232—237).—Starch can be estimated in fæces by the method already described (see preceding abstract) without treatment with hydrochloric acid and phosphotungstic acid, provided that the copper reducing power is determined gravimetrically.

Owing to the relatively large amount of pentosans and the small amount of hexosans in extracts of fæces it is essential to determine the pentosans.
N. H. J. M.

Estimation of Glycogen. ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1903, 37, 442—456).—Purely polemical. A reply to Pflüger (this vol., i, 72; ii, 247, and 248).
J. J. S.

Testing Fire-proof Wood. CHARLES F. MCKENNA (*J. Amer. Chem. Soc.*, 1903, 25, 406—414).—By means of electrical appliances, for which the original paper should be consulted, a retort containing a small quantity of wood is instantly brought to about 680° and kept at that temperature for two minutes. The gases evolved are collected and measured, and the residual charcoal may also be weighed. From a large number of experiments made by the author, it appears that the best fireproof woods are those which give off the smallest volume of gas and leave the most charcoal. Sometimes it is advisable to dry the samples and then expose them to the air long enough to reabsorb the normal amount of moisture.
L. DE K.

Use of Amyl Alcohol in Gerber's Method for the Estimation of Fat in Milk. J. VAN HAARST (*Zeit. angew. Chem.*, 1903, 16, 451—452).—Some kinds of amyl alcohol used in Gerber's process, although up to specification, are nevertheless unfit for use and may cause very serious discrepancies in the fat estimations. The only way to make sure whether the article is fit for Gerber's process is to see whether the results obtained agree with those obtained by a standard process, such as Thörner's.
L. DE K.

Comparison of Methods for Detecting Heated Milk. FRANZ LAUTERWALD (*Milch.-Zeit.*, 1903, 32, 241—242, and 262—263).—Storch's *p*-phenylenediamine test (compare Abstr., 1902, ii, 539) and that of Utz, who employs the substance "Ursol D" (compare Abstr., 1902, ii, 582), were found to be equally sensitive and trustworthy. Utz's test, however, was not interfered with to as great an extent as Storch's by the presence of added substances to the milk, such as ammonium thiocyanate. "Ursol D" is stated to be unpurified *p*-phenylenediamine.
W. P. S.

Renovated Butter. CHARLES A. CRAMPTON (*J. Amer. Chem. Soc.*, 1903, 25, 358—366).—Renovated butter is the product obtained by melting and settling butter unfit for food, removing any bad odour by means of a current of air, and churning the clarified fat with milk.

The author finds it as yet impossible to distinguish the article from genuine fresh butter by the ordinary chemical and optical means generally employed, but a clue may be often obtained by a microscopical test with polarised light, which will show that the fat has been melted. The "spoon test" and particularly the Waterhouse test, as described in the methods of the Association of Official Agricultural Chemists, also prove useful.

L. DE K.

Detection of "Saccharin" in Wines, Beers, &c. C. BOUCHER and F. DE BOUNGE (*Bull. Soc. chim.*, 1903, [iii], 29, 9, 411—412).—The sample is acidified with sulphuric acid and a 1 per cent. solution of potassium permanganate is added in slight excess, which is then removed by means of sulphurous acid. The filtrate is agitated with ether to extract the "saccharin," which is identified by the usual means.

The advantages claimed for this process are: the destruction of the tannin and salicylic acid, the latter of which particularly interferes with the test for "saccharin," and the destruction of the colouring and extractive matters. The liquid may now be shaken with ether without fear of the formation of a troublesome emulsion, and the extraction is complete within one hour. Permanganate does not act on "saccharin."

L. DE K.

Assay of Cantharides. EUGÈNE LÉGER (*J. Pharm. Chim.*, 1903, [vi], 17, 457—461).—Twenty-five grams of the powdered sample are placed in a wide-mouthed bottle and 125 c.c. of benzene and 2 c.c. of hydrochloric acid are introduced. The bottle is corked and then placed in an oven heated at 60—65° for 3 hours. When cold, the liquid is filtered through cotton-wool and the washings are collected separately. The benzene is then recovered by distillation, the operation being conducted in a weighed flask, and the washings are distilled first. The last traces of benzene are removed by a current of air. The fatty matter is removed by treatment with 10 c.c. of light petroleum boiling below 50°. The clear liquid is carefully passed through a small weighed filter, dried at 60—65°, and the crystals are washed 4 times with light petroleum, using altogether 24 c.c. The filter is then replaced in the flask, the whole is dried at 60—65° for one hour, and weighed.

L. DE K.

Sitosterol. A Possible Test for Maize Oil. AUGUSTUS H. GILL and CHARLES G. TUFTS (*J. Amer. Chem. Soc.*, 1903, 25, 254—256).—When testing cotton-seed oil for an admixture of maize oil, advantage may be taken of the high melting point of sitosterol acetate (127°).

The phytosterol acetate is prepared in the usual way, and then repeatedly crystallised from 95 per cent. alcohol, to which a few drops of water are added. If, finally, a product is obtained showing an abnormally high melting point, the presence of sitosterol may be suspected. Twenty, or even 10, per cent. of added maize oil may thus be detected.

L. DE K.

Estimation of Urea in Urine. OTTO FOLIN (*Zeit. physiol. Chem.*, 1903, 37, 548—550. Compare Abstr., 1902, ii, 630, and this vol., ii, 116).—Experiments show that creatine does not yield ammonia when boiled with magnesium chloride in acid solution and then distilled according to the process previously described for the estimation of urea (compare Arnold and Mentzel, this vol., ii, 48). J. J. S.

Complete Decomposition of Urea and Ammoniacal Salts by means of Nascent Sodium Hypobromite in an Alkaline Medium. OCTAVE LE COMTE (*J. Pharm. Chim.*, 1903, [vi], 17, 471—475).—It is a well-known fact that urea and even ammoniacal salts are not completely decomposed by recently prepared sodium hypobromite. The author has shown that all the nitrogen may be liberated by this substance in a nascent state in the presence of excess of alkali. The solutions required are (A) 20 grams of sodium hydroxide dissolved in 100 c.c. of water, and (B) a solution of 5 c.c. of bromine and 10 grams of sodium bromide in 100 c.c. of water.

1.2 c.c. of diluted urine (1:1) are introduced into a nitrometer and 2.4 c.c. of A, and afterwards 4 c.c. of B, are introduced. After 15 minutes, the volume of the nitrogen is read off with the usual precautions, and the urea is calculated from the result. Ammonium compounds may be estimated similarly. L. DE K.

Precipitation and Separation by Weak Organic Bases. EUGENE T. ALLEN (*J. Amer. Chem. Soc.*, 1903, 25, 421—444).—A lengthy paper of a physical and mathematical nature. The experiments were made with phenylhydrazine and aniline, which were added to various metallic solutions.

Aniline quantitatively precipitates titanium, zirconium, cerium, and thorium, as well as ferric iron, aluminium, and chromium, under certain conditions, from dilute and slightly acid solutions. The same applies to phenylhydrazine, except that ceric and ferric salts are reduced to lower oxides which are not, or only incompletely, precipitated. Zinc, cadmium, mercury, cobalt, and nickel form sparingly soluble additive products with phenylhydrazine. Similar compounds are obtained by the action of aniline on zinc, cadmium, and mercury. The strongly basic elements, magnesium, barium, calcium, strontium, manganese, and ferrous iron, are not precipitated. Beryllium alone is not precipitated by aniline or phenylhydrazine except from its sulphate solutions. The following separations were worked out: titanium and zirconium from iron; titanium, zirconium, and thorium from beryllium. Aluminium may be separated from ferrous iron by a double precipitation with phenylhydrazine; in fact, this is advisable in all these separations. In the case of beryllium, the separations may be effected equally well with aniline. L. DE K.

A Test for Hydrastinine. ARMAND JORISSEN (*Ann. Chim. anal.*, 1903, 8, 126).—The author has noticed that an aqueous solution of hydrastinine hydrochloride, which is already characterised by a fine

blue fluorescence, has the property of instantly reducing an alkaline solution of potassium mercuric iodide (Nessler reagent) in the cold and depositing a black precipitate of metallic mercury. Of the other alkaloids and glucosides, morphine, apomorphine, and picrotoxin also give this reaction.

L. DE K.

Estimation of Narcotine and Codeine in Opium. P. VAN DER WIELEN (*Chem. Centr.*, 1903, i, 938; from *Pharm. Weekblad.*, 40, 189—193).—*Narcotine*.—Three grams of opium powder are shaken with 90 c.c. of ether and 5 c.c. of 10 per cent. aqueous sodium hydroxide, 3 grams of calcium chloride are added, and after 24 hours 75 c.c. of the ethereal liquid are submitted to distillation until 60 c.c. have passed over. The residual ether is repeatedly agitated with 2.5 per cent. hydrochloric acid, the acid extract is filtered, rendered alkaline with sodium hydroxide, and again shaken with 25 c.c. of ether. Five grams of calcium chloride are added, the ethereal liquid is filtered, and after the ether has been expelled by evaporation, the residue is dissolved in 4 c.c. of hot 90 per cent. alcohol. The crystals of narcotine which separate in 24 hours are collected on a weighed filter, washed with 5 c.c. of alcohol, dried first in the air, afterwards at 100°, and weighed. A correction of 0.016 gram should be made for loss on account of solubility in alcohol.

Codeine.—The alcoholic mother liquor is mixed with 10 c.c. of water, the mixture evaporated to 10 c.c., and after 24 hours the liquid is filtered. The codeine is then estimated by adding 50 c.c. of *N*/100 acid and titrating back with *N*/100 alkali, using hæmatoxylin as indicator.

L. DE K.

Indicators for the Titration of Cinchona Alkaloids. J. MESSNER (*Zeit. angew. Chem.*, 1903, 16, 441—450, 468—477).—The author has tested the various indicators recommended for the purpose of titrating the cinchona alkaloids and found most of them to be unsuitable. For the estimation of mixed alkaloids, the following process is recommended.

One gram of cinchona extract is dissolved in 10 c.c. of water and 5 c.c. of absolute alcohol and shaken with 95 c.c. of ether and 10 c.c. of aqueous soda. Fifty c.c. of the ethereal layer are then heated in a distilling apparatus until about 2 c.c. are left, and this is at once diluted with 40 to 50 c.c. of alcohol. The alkaloids are then titrated with *N*/10 hydrochloric acid with pure lacmoid as indicator.

A 5 per cent. solution of sodium dihydrogen phosphate is recommended as a test for distinguishing quinine from the other cinchona alkaloids, as its 1 per cent. neutral solution soon yields a crystalline precipitate of quinine phosphate, whilst the others are not precipitated. Disodium hydrogen phosphate, however, precipitates cinchonine but not cinchonidine, and gives a transient turbidity with quinine or quinidine.

L. DE K.

New Method for the Estimation of Tannins. PAUL FELDMANN (*Chem. Centr.*, 1903, i, 1048—1049; from *Pharm. Zeit.*, 48, 255—257).—It is proposed to titrate tannin with solution of bleaching

powder in the presence of sulphuric acid and excess of indigo, the end reaction being indicated by the disappearance of the blue colour. The method is said to give concordant results. Gallic acid counts as tannin. The presence of sugar, glycerol, and alcohol do not interfere with the process, but salicylic acid is oxidised. L. DE K.

The "Biological" Test for Blood. G. S. GRAHAM-SMITH and F. SANGER (*J. Hygiene*, 1903, 3, 258--291).—The biological or precipitin test for human blood has in forensic practice been ignored in this country, although not abroad. The present paper goes into many details of the test, such as the quantitative application of the method, and the interference with the test when the blood has been mixed with other substances, or dried on various fabrics. For instance, leathers are mostly acid, and extracts of acid reaction give a precipitate with blood; after neutralisation the test can be applied; if the blood is, however, dried on thick, polished, yellow leather, it is impossible to obtain the blood test. W. D. H.

Relation of the Specific Gravity of Urine to the Solids Present. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1903, 25, 257—262).—A large number of experiments showing that the percentage of solids in urine may generally be calculated with sufficient accuracy from a careful determination of the specific gravity, as already recommended by Neubauer and others.

The new factor proposed is 0.26 when the sp. gr. is taken at $25^{\circ}/4^{\circ}$, and 0.234 when taken at $20^{\circ}/4^{\circ}$. L. DE K.

Reaction of Urochrome with Acetaldehyde. ARCHIBALD E. GARROD (*J. Physiol.*, 1903, 29, 335—340).—When acetaldehyde is added to an alcoholic solution of urochrome, a urobilin-like substance is formed. This, however, is not observed with all specimens of acetaldehyde, and the reaction is due to some other substance mixed with the acetaldehyde and formed from it under the influence of light and warmth. What this substance is, is not yet made out. In the course of the reaction, two products are formed, one more slowly than the other. Both show absorption bands. The reaction points to a relationship of urochrome to hæmatin and to bilirubin, and supplies a delicate test for urochrome. W. D. H.

[Analysis of] Civet. HERBERT E. BURGESS (*Analyst*, 1903, 28, 101—104).—Vaselin having been recently detected in various samples of commercial civet, the following method is proposed for estimating this adulterant. Five grams of the sample are treated with 50 c.c. of cold acetone, filtered, the residue washed with a further 50 c.c. of acetone, and then extracted with 50 c.c. or more of light petroleum. After filtration, the petroleum solution is evaporated, dried, and weighed. The author has found 1.8 to 7.24 per cent. of vaselin in different samples of civet, whilst genuine samples only yielded from 0.25 to 0.4 per cent. of matter soluble in light petroleum. Other adulterants found were butter, lard, soft soap, and various other fats. W. P. S.

General and Physical Chemistry.

A Hand-spectroscope for Chemists. ERNST BECKMANN (*Ber.*, 1903, 36, 1984—1987).—The special advantage of the spectroscope described is that the scale is brightly illuminated by a small $3\frac{1}{2}$ -volt electric lamp placed in a tube parallel to the observation tube, the light being reflected on to the scale by a mirror. The accurate comparison of two spectra on the scale is thus rendered possible.

W. A. D.

Spontaneous Dichroism of Mixed Liquids. GEORGES MESLIN (*Compt. rend.*, 1903, 136, 1641—1643. Compare this vol., ii, 408).—A mixture of potassium chlorate in amyl alcohol exhibits a strong dichroism in a magnetic field, which persists for some time after the field has been cut off because the orientation of the crystalline plates is not at once destroyed.

In even a weak magnetic field, produced by a bar magnet, this mixture polarises light, and the polarising power remains after the magnet is removed. This action on light, different in the horizontal and vertical directions, is not due to terrestrial magnetism, but is to be attributed to gravity, which causes the suspended particles to set in definite order. According to the way in which the particles are oriented, the dichroism may be positive or negative, and under the influence of a magnetic field it may change its sign. The phenomenon has been observed with potassium chlorate in amyl alcohol, butyl alcohol, and phenol, with potassium carbonate in amyl alcohol and light petroleum, and with boric acid in amylene, light petroleum, chloroform, turpentine, carbon disulphide, benzene, toluene, xylene, cumene, and styrene. The spontaneous and the magnetic dichroisms have the same sign in the cases of potassium carbonate and chlorate, but inversion takes place in the mixtures of boric acid with the liquids mentioned. Those mixtures which are spontaneously dichroic are those which are most actively dichroic in a magnetic field.

J. McC.

Influence of Solvents on the Rotatory Power of Certain Molecules. Derivatives of Camphor. ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1903, 136, 1525—1529. Compare this vol., i, 503).—In order to determine the influence of the solvent in causing the enolisation (production of double linking), the rotatory powers of cyanocamphor and of camphocarboxylic acid and its methyl, propyl, and *isobutyl* esters were determined in solutions in various solvents. In benzene and its homologues, the specific rotation of cyanocamphor is very low; in ionising solvents, the rotatory power increases, and in solutions of sodium hydroxide may even attain such a high value as

+132°. The influence of the ionising power of the solvent is also evident in the other cases. When sodium is dissolved in the benzene used as solvent for the esters of camphorcarboxylic acid, the rotatory power is enormously increased; methyl camphorcarboxylate has $[\alpha]_D$ +21.12° in benzene, but if sodium amounting to 11 per cent. of the weight of the ester be dissolved in the benzene so as to give a 0.9 per cent. solution, $[\alpha]_D$ increases to +121.5°. In all these cases, the increase is attributable to a change of the complex $\begin{array}{c} \text{CHR} \\ \diagdown \\ \text{CO} \end{array}$ into



The following results illustrate the influence of the double linking on the rotatory power :

	Benzene.	Alcohol.	Acetic acid.	Methyl iodide.	Alcohol and sodium.
Cyanomethylcamphor (ketonic form).....	$[\alpha]_D = 93.7^\circ$	93.7°	93.7°	95.7°	—
Cyanomethylcamphor (enolic form)	$[\alpha]_D = 146$	156.2	177	165.6	154°
Cyanopropylcamphor (enolic form)	$[\alpha]_D = 94.12$	100	103.12	—	—
Methyl allylcamphor- carboxylate.....	$[\alpha]_D = 33.25$	56.88	56.88	—	56.88

These results also show that benzene exerts a depressing effect on the rotatory power of these compounds. J. McC.

Influence of the Introduction of Unsaturated Radicles on the Rotatory Power of Active Molecules. ALBIN HALLER and MARCEL DESFONTAINES (*Compt. rend.*, 1903, 136, 1613—1616).—See this vol., i, 628.

Phosphorescence of Calcium Sulphide containing Bismuth in presence of Traces of Sodium. L. E. O. DE VISSER (*Rec. trav. chim.*, 1903, 22, 133—138. Compare Abstr., 1902, ii, 237).—It is here shown that calcium sulphide containing bismuth, prepared from pure calcium carbonate, and free from traces of sodium is not phosphorescent; it becomes so, however, when small quantities of sodium are added, a maximum of activity being reached when there is present 1 atom of sodium per 800 mols. of calcium sulphide. The amount of bismuth which produces the maximum phosphorescence (*loc. cit.*) appears to be independent of the proportion of sodium present, and is approximately 1 atom of bismuth per 50,000 of calcium.

W. A. D.

Hypothesis of the Nature of Radioactive Substances. FILIPPO RE (*Compt. rend.*, 1903, 136, 1393—1395).—The author regards it as natural to suppose that the particles constituting the atoms were originally in a free state and formed a nebulous medium

of great tenuity. Subsequently they united about centres of condensation and gave rise to infinitely small suns, and by a further process of contraction they have assumed stable and definite forms, and these are the atoms of the elements we know. The larger suns, which have not yet undergone the further process of contraction, are the atoms of radioactive substances. This hypothesis accounts for the high atomic weight possessed by radioactive substances, and for the development of energy by them, which is due to a contraction of their atoms. Many of the phenomena exhibited by radioactive substances do not differ from those shown by the sun, for instance, luminous, calorific, and actinic radiation and discharge of electrified particles. Rain and snow, freshly fallen, are radioactive, and it does not seem improbable that their radioactivity is due to the action of solar light. The influence of a magnetic field on radioactive radiation differs from that on solar radiation, but the conditions of observation are entirely different.

J. McC.

A Property of the α -Rays of Radium. HENRI BECQUEREL (*Compt. rend.*, 1903, 136, 1517—1522. Compare this vol., i, 257).—A radium salt was placed in a lead tube, and this was closed by an aluminium plate to arrest the light emitted. Above this a screen was placed, and over it a photographic plate lying horizontally, the whole system being oriented parallel to a strong magnetic field. Provided the exposure is not too long, no appreciable impression is produced by the γ -rays. If in the middle of the exposure the direction of the magnetic field is reversed, an impression of two parallel tracks is produced on the plate. If the plate be placed at an angle instead of horizontally, the tracks are curved and meet at the point of contact of the plate and the screen.

It might be that these curves were segments of circles in accordance with the ballistic theory. In this case, it was to be expected that the relationship $RH = mv/e$ would hold good as it does for the β -rays, where R is the radius of the circular trajectory, H is the intensity of the magnetic field, m is the mass carrying charge e , and v is the velocity. The results obtained for RH when the distance of the plate from the screen is varied are not constant, but vary from 1.9 to 2.9×10^5 . This inconstancy may well be explained by variation of the mass m . It is certain, however, that the curvature of the trajectory of the α -rays increases with the length of the trajectory, and the disturbance is no doubt due to the presence of the air. In a vacuum, RH would probably be constant. If we assume m to be a material mass positively charged, then on passing through the air it attracts the negative ions of the air and the charge e diminishes.

If m be assumed to be merely an electromagnetic magnitude dependent on e and v , it may likewise be admitted that the charge e attracts the negative ions of the air and thus alters the trajectory.

This suggested explanation is supported by the fact that the α -rays of radium are absorbed when they pass through air, and they become less and less penetrating as they pass through increasing thicknesses of aluminium.

J. McC.

Action of Cathode Rays on Inorganic and Organic Substances. EUGEN GOLDSTEIN (*Ber.*, 1903, 36, 1976—1984).—If Elster and Geitel's assumption (*Ann. Phys. Chem.*, 1896, [ii], 59, 487) is true that the colour of metallic chlorides which have been exposed to the cathode rays is due to a subchloride formed by the liberation of halogen, ammonium salts should remain colourless when subjected to the rays; but it is found that, at the temperature of liquid air, ammonium chloride becomes greenish-yellow, ammonium bromide yellowish-brown, the iodide olive-brown, and the fluoride deep blue. The colour disappears when the temperature is raised and the product exposed to daylight. Tetra-alkylammonium halogen salts behave similarly, giving various shades of colour, and yellow to green shades are also obtained with substances such as chloroacetic, trichloroacetic, and bromoacetic acids, bromoform, and chloral, which contain a halogen. On the other hand, acetic acid and aldehyde remain colourless, so that the colour of the ammonium salts and of the substituted compounds is apparently produced by the halogen. That the metal in metallic salts also helps in the production of colour is, however, shown by Giesel's results (*Abstr.*, 1897, ii, 170). It should be noted that the halogen in these cases must have its power of absorbing light enormously increased by the cathode rays, as it is known that the halogens, including iodine (in very dilute solution), are colourless at the temperature of liquid air.

Sulphur, which at low temperatures is perfectly white, becomes bright chamois-coloured in the cathode rays; the colour becomes very faint in daylight, even in liquid air, and rapidly disappears when the temperature is raised. The change here produced by the rays must be that of one allotropic form to another.

The following colourless compounds also become coloured in the cathode rays when cooled in liquid air; sulphuric monohydrate (saffron-yellow), concentrated hydrochloric acid (green), phosphoric acid (hyacinth-red), hydrobromic acid of sp. gr. 1.49 (intense green), chloric acid (chamois), phosphorus pentachloride (bright yellow). W. A. D.

Galvanic Elements with Two Liquids: Electromotive Forces; Condensations; Transformation of Energy at the Electrodes. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 136, 1497—1505. Compare *Abstr.*, 1902, ii, 375, 376, 439, 440, 546, 591; this vol., ii, 3, 258, 259, 464).—The author discusses the results previously recorded in connection with galvanic elements. In systems where the *E.M.F.* of a galvanic element with liquids *A* and *B* is equal to the sum of the *E.M.F.* of *A + AB* and *B + AB*, since the *E.M.F.* does not vary with the nature of the electrodes, it is deduced that it is developed at the surface of contact of the two liquids. It is also shown that the *E.M.F.* is proportional to the heat change of the chemical reaction.

In these elements, it has been frequently noticed that although a continuous current can be obtained from them, the *E.M.F.* is not constant. In some cases, it does not at once rise to its maximum value, and in other cases it decreases when external work is being done by the cell. This variation is due to two causes: a condensation, depend-

ent on the velocity of the chemical reaction and on the electrical capacity of the system, and a progressive change in the composition of the two liquids; the second cause is particularly active when the liquids are merely separated by a porous division. The condensation which takes place is determined by the capacity of the electrodes and the vessels; its occurrence shows the necessity of waiting for a few minutes after the cell has been constructed before the *E.M.F.* is determined, so as to allow the equilibrium to be established. A certain part of the decrease of *E.M.F.* is due to leakage of electricity into the air; this tends to produce a certain electrical opposition between the two liquids and between the electrodes, which, of course, gives rise to polarisation effects.

Attention is directed to certain results obtained with an element containing sulphuric acid and sodium hydroxide solutions. The *E.M.F.* falls when the cell is in use, but rises to nearly its original value after the circuit has been broken for some time. Since the rise to the original value is rapid, it follows that the diminution cannot be attributed to polarisation. The explanation offered is that on account of insufficient diffusion the chemical reaction cannot keep up with the expenditure of electrical energy whilst external work is being done. On account of the high velocity of the chemical reaction in the oxidation process, a cell made up of an alkaline solution of pyrogallol and one of hydrogen peroxide solution containing sodium chloride maintains its *E.M.F.* practically constant.

The *E.M.F.* in these cells is not always proportional to the heat change of the chemical reaction; thus, the heat change of the reaction between sodium hydroxide (0.2*N*) and nitric acid (0.2*N*) at 15° would correspond with an *E.M.F.* of about 0.55 volt and with a slightly higher *E.M.F.* at 54°, whereas at 15° the *E.M.F.* is 0.55 volt, but at 54° it is 0.78 volt. These variations are attributed to energy transformations which take place at the electrodes. Possibly the metals of the electrodes suffer some change of structure, or they isomerise, as is known to be the case with silver. In instances of this kind, there may be an increase of potential with a diminution of the energy transmitted.

J. McC.

Galvanic Elements with One and with Two Liquids. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 136, 1601—1608).—Three elements can be constructed with a solution of an electrolyte and three metals. If the metals be represented by *M*, *M'*, and *M''*, and the solution by *A*, the elements are: *MAM'*, *MAM''*, and *M'AM''*. Using zinc, copper, and platinum, it has been proved that the *E.M.F.* of the cell with a zinc and a platinum electrode is equal to the sum of the *E.M.F.* of the element with a zinc and a copper electrode and that of the element with a copper and a platinum electrode. In each case, the platinum (or the copper in the case of a zinc and a copper electrode) was the positive electrode. The same relationship was found to hold good in a solution containing a mixture of salts.

With two solutions, *A* and *B*, and three metals, nine elements can be constructed: *M | A + B | M*, *M' | A + B | M'*, *M'' | A + B | M''*, *M | A + B | M'*, *M | A + B | M''*, *M' | A + B | M''*, *M | B + A | M'*,

$M | B + A | M''$, and $M' | B + A | M''$. It has been proved that the sum (algebraic) of the *E.M.F.* of two reciprocal elements with different metallic electrodes, $M | A + B | M'$ and $M' | B + A | M$, is equal to the sum of the *E.M.F.* of two elements with the same electrodes, $M | A + B | M$ and $M' | A + B | M'$. The experiments were made with solutions of sulphuric acid and sodium hydroxide, zinc sulphate and sodium sulphate, boric acid and sodium hydroxide, boric acid and sulphuric acid, sodium borate and ammonium chloride, and ammonium borate and sodium chloride; zinc, copper, and platinum were used as electrodes.

J. McC.

Potential Differences with Saturated Solutions. DOUGLAS MCINTOSH (*J. Physical Chem.*, 1903, 7, 348—355).—It was shown, thermodynamically, by Luther (Abstr., 1896, ii, 461), that changing the solvent at one electrode should have no effect on the *E.M.F.* of a two-solution cell if the solutions were saturated. This was afterwards shown to be invalid if the solute were a hydrated salt. The author proves experimentally that the *E.M.F.* is not zero for a two-fluid cell containing solutions of mercurous and potassium chlorides in water and in alcohol, both methyl and ethyl alcohols being employed. Saturated solutions of silver nitrate in alcohol and water also yielded a measurable *E.M.F.* The mistake, in the author's opinion, lies in the assumption of the law "if two systems are in equilibrium with a third they are in equilibrium with one another," which is only true for non-miscible phases.

L. M. J.

A New General Relationship between the Electromotive Forces of Salt Solutions. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 136, 1357—1373).—The law already developed (compare this vol., ii, 258) concerning the *E.M.F.* produced by the action of an acid on a base, and of a salt on the corresponding acid and base, appears as a special case of a more general law. If the *E.M.F.* of an element consisting of solutions of two salts, *A* and *B*, separated by a porous division is *E*, that of the element made up of solutions of *A* and *AB* is ϵ_1 , and that of the element with solutions of *B* and *AB* is ϵ_2 , it is found that $E = \epsilon_1 + \epsilon_2$.

This has been proved for six different types. The law does not obtain in those cases where gaseous products or insoluble substances separate at the electrodes, but this is easily accounted for by polarisation.

The *E.M.F.* of the three systems was determined, and in practically all cases it was found that $E = \epsilon_1 + \epsilon_2$. In most cases, the experiments were carried out with various metals (platinum, copper, mercury, and zinc) as electrodes.

First Family.—Salts of strong acids; the mixtures being thermally neutral. The mixtures examined were: (1) $A = \text{ZnSO}_4$, $B = \text{CuSO}_4$, $AB = \text{ZnSO}_4, \text{CuSO}_4$; (2) $A = \text{ZnCl}_2$, $B = \text{CuSO}_4$, $AB = \text{ZnCl}_2, \text{CuSO}_4$; and (3) $A = \text{HgCl}_2$, $B = \text{Hg}(\text{CN})_2$, $AB = \text{HgCl}_2, \text{Hg}(\text{CN})_2$. The small divergencies observed are easily attributable to polarisation effects. In these cases, there is scarcely any thermal change on mixing the salt solutions, and consequently the external energy developed is mainly derived from the surrounding medium.

Second Family.—Salts of weak acids. When solutions of these salts are mixed, there is a considerable thermal change. The cases examined were: (1) $A = 2\text{NH}_4\text{Cl}$, $B = \text{Na}_2\text{B}_4\text{O}_7$, $AB = 2\text{NH}_4\text{Cl}, \text{Na}_2\text{B}_4\text{O}_7$; (2) $A = \text{NaCl}$, $B = (\text{NH}_4)_2\text{B}_4\text{O}_7$, $AB = \text{NaCl}, (\text{NH}_4)_2\text{B}_4\text{O}_7$; (3) $A = \text{NaCl}$, $B = (\text{NH}_4)_2\text{CO}_3$; and (4) $A = \text{NH}_4\text{Cl}$, $B = \text{Na}_2\text{CO}_3$. In every instance, $E = \epsilon_1 + \epsilon_2$ within the limits of experimental error.

Third Family.—Acid and normal salt of a strong acid. The following were examined: $A = \text{HCl}$, $B = \text{NaCl}$; $A = \text{H}_2\text{SO}_4$, $B = \text{Na}_2\text{SO}_4$; $A = 2\text{HCl}$, $B = \text{Na}_2\text{SO}_4$; $A = \text{H}_2\text{SO}_4$, $B = \text{NaCl}$; and $A = \text{HCl}$, $B = \text{NH}_4\text{Cl}$. The general relationship was also evident in these cases. In the first four cases, the *E.M.F.* developed in the element $A + B$ is nearly the same. It is also worthy of note that the *E.M.F.* of the element $A + B$ is very nearly the same as that of the system $B + AB$, whilst the system $A + AB$ gives only a very low *E.M.F.*

Fourth Family.—Base and normal salt of a strong acid. The thermal change in these cases is small, yet a comparatively high *E.M.F.* is developed, and the general relationship obtains, as was proved with: $A = \text{NaCl}$, $B = \text{NaOH}$; $A = \text{NH}_4\text{Cl}$, $B = \text{NH}_3$; and $A = \text{NH}_4\text{Cl}$, $B = \text{NaOH}$. The *E.M.F.* of the system $A + AB$ is almost the same as that of the system $A + B$, but very small values are obtained for the system $B + AB$. In the last case, excess of base is almost without influence on the *E.M.F.*

Fifth Family.—Double salts stable in the dissolved condition. The relationship holds good in these instances also, as was proved by experiments with: $A = \text{Hg}(\text{CN})_2$, $B = 2\text{KCN}$, the thermal reaction is $\text{Hg}(\text{CN})_2$ (dissolved) + 2KCN (dissolved) = +12.4 Cal.; $A = \text{HgCl}_2$, $B = 2\text{KCN}$, where 17.0 Cal. are developed when solutions of the salts are mixed; $A = \text{Hg}(\text{CN})_2$, $B = 2\text{KCl}$; $A = \text{HgCl}_2$, $B = 2\text{KCl}$. When platinum or copper electrodes were used, the results were not quite satisfactory, for some mercury deposited on the electrodes, which caused a dissociation of the complex ion, and consequently a change in the constitution of the solution. It was also proved that six elements made up of HgCl_2 and 2KCN could produce visible electrolysis in a voltameter containing dilute sulphuric acid and pyrogallol under a pressure of 0.012 m. These results prove that the heat developed by the formation of double salts which are stable in presence of water can be utilised in carrying out external electrolysis.

Sixth Family.—Oxidation elements. The relationship has been verified in the case of galvanic elements constructed from: $A = 2\text{FeSO}_4 + \text{H}_2\text{SO}_4$, $B = \text{H}_2\text{O}_2$, $AB = \text{Fe}_2(\text{SO}_4)_3$. The thermal change is: $(2\text{FeSO}_4 + \text{H}_2\text{SO}_4)$ (dissolved) + H_2O_2 (dissolved) = $\text{Fe}_2(\text{SO}_4)_3$ (dissolved) + 62.2 Cal. J. McC.

Influence of Dissolved Gases on Conductivity for a Direct Current. SAMUEL L. BIGELOW (*J. Physical Chem.*, 1903, 7, 327—347. Compare this vol., ii, 128).—The author has investigated the currents obtained in an electrolytic cell with *E.M.F.* less than that necessary for the decomposition of the electrolyte; the currents were measured shortly after the closing of the circuit and before they had reached the condition of "residual currents." It was found that heating the electrodes to redness formed an effective method of destroying pre-

vious polarisation. The electrolyte employed was $N/200$ H_2SO_4 , and it was found that the strength of the current increased greatly with the presence of dissolved gases. Thus, if the current through the air-free electrolyte be taken as unity, that through the electrolyte when saturated with air is about 19, when saturated with oxygen about 60, when saturated with nitrogen about 7, when saturated with hydrogen about 52, and when saturated with carbon dioxide less than unity. The current is slightly less in each case for a normal sulphuric acid solution, indicating that the conductivity is not due to the ions of the electrolyte. The current obtained with pure water is somewhat lower than that of the sulphuric acid, but the increase when air is dissolved is far less than that in the case of the acid solution, although carbon dioxide causes a great increase. These results appear to show that if the conductivity is due to the dissolved gas, it is also dependent on the presence of an electrolyte. Although as yet a complete explanation is not possible, the author points out that these results should not be considered as opposed to the dissociation theory, as they apply to a different group of facts not satisfactorily explained by this theory. L. M. J.

Saturated Aqueous Solutions of Difficultly Soluble Salts.

I. Electrical Conductivity. FRIEDRICH KOHLRAUSCH [with F. ROSE and FRIEDRICH DOLEZALEK] (*Zeit. physikal. Chem.*, 1903, 44, 197—249. Compare Kohlrausch and Rose, Abstr., 1894, ii, 7; Kohlrausch and Dolezalek, Abstr., 1902, ii, 72).—Full details are given of the measurement of the conductivity for solutions of 41 sparingly soluble salts. Some of the results have been published already (*loc. cit.*). J. C. P.

Electrolytic Solution of Platinum by Alternating Currents.

RUDOLF RUER (*Zeit. physikal. Chem.*, 1903, 44, 81—113).—Details are given of work already described (see this vol., ii, 407).

J. C. P.

Electrolysis of Aqueous Solutions. CARL FRENZEL (*Zeit. Elektrochem.*, 1903, 9, 487—496).—When solutions of ammonia or of the hydroxides of the alkalis or alkaline-earths are electrolysed with an unpolarisable cathode and a small anode, a gradually increasing *E.M.F.* being employed, the curves representing the connection between the current passing and the applied *E.M.F.* exhibit a change of direction corresponding with the discharge of hydroxyl ions; after this, the current increases with increasing *E.M.F.*, it then remains constant or diminishes, and finally increases again. The *E.M.F.* at which the second increase begins, varies with the concentration of the hydroxyl ions in the solution; when the latter is divided by 10, the *E.M.F.* rises by 0.06 volt. The form of curve described above is only obtained when the anode is a platinum wire freshly heated to redness; when the same wire is used repeatedly, the successive curves become more and more continuous, finally exhibiting a steady rise of current with rising *E.M.F.* The change is much more marked in solutions of ammonia than it is in the other solutions. It is shown that the impurities in the salts used have no effect on the form of the

curves, and also that the assumption of a transition resistance at the anode due to a layer of gas does not account for it. The assumption of some chemical change at the anode is therefore necessary. The most probable is the formation of ozone by interaction of discharged hydroxyl ions and molecular oxygen occluded by the electrode. This is capable of explaining the effect of heating the anode to redness, and also the dependence of the position of the change of direction on the concentration of the hydroxyl ions in the solution. T. E.

Classification of Liquids and Crystals from a Magnetic Point of View. GEORGES MESLIN (*Compt. rend.*, 1903, 136, 1438—1440. Compare this vol., ii, 408, 521).—The author finds that crystalline substances may be divided into two classes according to the positive or negative character of the dichroism induced in their suspensions in a selected liquid, when these are placed in a magnetic field (*loc. cit.*). Liquids may be divided similarly according to whether their mixtures with a selected crystalline substance are positively or negatively dichroic in a magnetic field. A preliminary classification of this kind for a number of liquids and solids is given in the original. T. A. H.

Permanent Changes and Thermodynamics. IX. PIERRE DUNEM (*Zeit. physikal. Chem.*, 1903, 43, 695—700).—A theoretical paper, not suitable for abstraction. J. C. P.

Dissociation Curves. ALBERT BOUZAT (*Compt. rend.*, 1903, 136, 1395—1397).—The dissociation pressures at several temperatures have been determined for a number of solid substances which dissociate into solid and gaseous substances, and the results have been compared with those obtained by Troost (*Abstr.*, 1879, 501) for the compound $\text{NH}_4\text{Cl}, 3\text{NH}_3$.

If Q_T is the quantity of heat absorbed by the separation of 1 mol. of gas at the temperature T , it can be shown by applying Clapeyron's formula that if Q_T/T in two univariant systems has the same value for a particular pressure, the ratio T'_B/T'_A of the absolute temperatures corresponding with the same pressure in the two systems is constant whatever be the pressure; and inversely, if T'_B/T'_A is constant at all pressures, the value of Q_T/T has the same value for any particular pressure in the two systems A and B . The results obtained confirm this deduction.

The results also show that if all the univariant systems in which a solid gives rise by dissociation to another solid and a gas be arranged in a group, the ratio of the temperatures corresponding with the same dissociation pressure of any two systems of the group is constant whatever be the pressure. This law shows that the whole of the dissociation curve of a system (univariant) may be traced if a single point is determined.

Since Q_T/T represents the variation of entropy, it follows that if these univariant systems be arranged as before, in a group, the varia-

tion of entropy which results from the liberation of 1 mol. of gas at a determinate pressure is the same for all the systems of the groups.

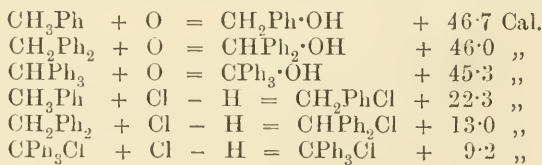
The experiments were made with: AgCl , 1.5NH_3 ; ZnCl_2 , 6NH_3 ; CuSO_4 , $5\text{H}_2\text{O}$; Pb_3O_4 ; and BaO_2 . J. McC.

Phenyl-substitution in the Phenylmethanes, their Carbinols and Chlorides. JULES SCHMIDLIN (*Compt. rend.*, 1903, 136, 1560—1562).—The following heats of combustion have been determined, and from these values the heats of formation from the elements have been calculated:

	Heat of combustion at constant		Heat of formation.
	volume.	pressure.	
Toluene	937.4 Cal.	938.5 Cal.	− 2.4 Cal.
Diphenylmethane	1658.2 „	1659.9 „	− 20.0 „
Triphenylmethane.....	2385.1 „	2387.3 „	− 43.6 „
Tetraphenylmethane.....	3101.2 „	3104.1 „	− 56.6 „
Benzyl alcohol	890.9 „	891.8 „	+ 44.3 „
Diphenylcarbinol	1612.5 „	1613.9 „	+ 26.0 „
Triphenylcarbinol	2340.0 „	2342.0 „	+ 1.7 „
Benzyl chloride.....	885.7 „	886.6 „	+ 19.9 „
Chlorodiphenylmethane.....	1615.9 „	1617.3 „	− 7.0 „
Chlorotriphenylmethane ...	2346.5 „	2348.5 „	− 34.9 „

From these heats of formation, it can be seen that the thermal effect of the substitution by the phenyl group is not constant, but varies with the character of the compound in which the substitution takes place.

From the following table, the thermal changes which take place in the formation of carbinols or of chlorine substitution products are seen to diminish as the number of phenyl groups present increase:



J. McC.

Vapour Pressures of Ternary Mixtures. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1903, 43, 671—685. Compare Abstr., 1901, ii, 146, 224, 305, 372, 436, 641).—A theoretical discussion of some points of difference between the author's results and those of Ostwald (*Abhandl. K. Sächs. Ges. Wiss.*, 1900, 25, 413).

J. C. P.

Osmotic Pressure. A. SMITS (*Rec. trav. chim.*, 1903, 22, 153—158).—A theoretical paper emphasising the view that in solution there is no “essential difference between the solvent and the dissolved substance.” W. A. D.

Displacement of Osmotic Equilibrium by Surface Tension. FELIX KAUFLEDER (*Zeit. physikal. Chem.*, 1903, 43, 686—694).—The paper is almost entirely mathematical. With the help of the formulæ obtained, it is possible to predict approximately the excess concentration within cotton fibres immersed in the solution of a dye.

J. C. P.

Dissociation in, and Crystallisation from, a Solid Solution. CORNELIS A. LOBRY DE BRUYN and C. L. JUNGUS (*Proc. K. Acad. Wetensch. Amsterdam*, 1903, 5, 643—646).—From the change in colour which takes place when *o*-nitrobenzaldehyde is exposed to sunlight (*Ciamician and Silber, Abstr.*, 1901, i, 547), it is assumed that the *o*-nitrosobenzoic acid formed remains at first in solid solution, and to judge from the green colour it is in the unimolecular condition. Further exposure to sunlight causes change with deepening in colour until the saturation point is reached; the nitrosobenzoic acid then crystallises out, and the mass becomes lighter in colour, owing probably to a change to the bimolecular acid, which is white. The amount of *o*-nitrosobenzoic acid formed after definite intervals of exposure has been determined, but on account of the inconstancy of the light it is not possible to ascertain the velocity of the transformation. The saturated solution contains about 2.6 mols. of acid per 100 mols.

J. McC.

Polymerisation of Organic Liquids. G. G. LONGINESCU (*Ann. Sci. Univ. Jassy*, 1903, 2, 126—130).—The author has found that for a large number of organic liquids the relationship $T/D = \sqrt{n}$ constant holds, T denoting the absolute boiling point, D the density at 0°, and n the number of atoms in the molecule; the value of this constant is about 100, and hence the equation $T/100D = \sqrt{n}$, gives a means of determining the degree of aggregation in the case of polymerised molecules. Tables are given showing the agreement between the calculated values for the number of atoms in the molecule and those deduced from the formula. In the case of polymerised molecules, the degree of association calculated by this method agrees in many cases closely with that obtained by Ramsay's method of capillary ascension; thus for methyl, ethyl, and propyl alcohols, acetone, and nitroethane, the values for the degree of polymerisation, 3.1, 2.2, 1.7, 1.6, 1.4, are obtained instead of 3.4, 2.7, 2.2, 1.3, 1.5, as given by Ramsay. Acetonitrile as a liquid apparently exists as $(\text{CH}_3 \cdot \text{CN})_3$. W. A. D.

Solubility of Homogeneous Mixtures. Mixed Depolarisers. ALFRED THIEL (*Zeit. physikal. Chem.*, 1903, 43, 641—670. Compare Küster, *Abstr.*, 1899, ii, 205; Küster and Thiel, *Abstr.*, 1900, ii, 255; this vol., ii, 136; Thiel, *Abstr.*, 1900, ii, 521).—The author discusses various cases of homogeneous mixtures in relation to their solubility, and illustrates each as far as possible. The question is that of the way in which the solubility varies with the composition of the solid mixture. The following are the chief cases distinguished by the author. I. The two components are completely miscible, and the

solubility curve is a straight line joining the solubility points for the components; in other words, the change in solubility is proportional to the change in composition of the solid. This case is illustrated by silver chloride and bromide, potassium and rubidium permanganates, *p*-dichlorobenzene and *p*-dibromobenzene, and possibly potassium permanganate and perchlorate. II. The solubility curve exhibits a maximum. Cases cited here are β -naphthol and naphthalene (Küster, Abstr., 1895, ii, 439), lead and barium formates. III. The solubility curve exhibits a minimum. IV. The miscibility of the components is limited, and the solubility of the mixtures is intermediate between the solubilities of the components. To the gap in the mixture series there corresponds a horizontal line in the solubility curve. An example of this is furnished by mixtures of silver bromide and iodide (Thiel, *loc. cit.*). V. The miscibility of the components is limited, and the solubility of the saturated mixture is greater than that of either component. Examples of this case are furnished by potassium and thallium chlorates, ammonium and potassium bromides, potassium and thallium nitrates.

A number of subordinate and complicated cases are also discussed in the paper.

J. C. P.

Influence of Foreign Substances on the Solubility of Phenylthiocarbamide and of Boric Acid in Water. PETRU BOGDAN (*Ann. Sci. Univ. Jassy*, 1903, 2, 95—118).—Values are given showing the increase of solubility of phenylthiocarbamide in water caused by the addition of non-electrolytes such as carbamide, sucrose, ethyl and propyl alcohols, and acetone. With these substances, the value of the molecular constant $C = L_1 - L_0/a$, where L_0 is the solubility in pure water, L_1 the solubility in water containing a gram-mols. of the non-electrolyte, is sensibly the same in dilute solution. Electrolytes such as potassium and sodium nitrate diminish the solubility of the thiocarbamide, the effect of the former being greater than that of the latter.

The solubility of boric acid in water, on the other hand, is increased by both electrolytes and non-electrolytes alike; in the case of electrolytes, the solubility increases as the strength of the acid of the salt diminishes, and it is thus shown that a true chemical change is here involved.

A long theoretical discussion of Jahn's and Nernst's theories is included in the paper.

W. A. D.

Precipitation of Colloidal Solutions by Electrolytes. HERBERT FREUNDLICH (*Zeit. physikal. Chem.*, 1903, 44, 129—160. Compare Linder and Picton, *Trans.*, 1895, 67, 63; Hardy, *Abstr.*, 1900, ii, 396; Spring, *Abstr.*, 1900, ii, 713).—Colloidal solutions of arsenious sulphide, ferric hydroxide, and platinum were employed in this investigation, and the precipitating power of various salts was compared by determining the concentration of the salt solution that, within a given time and under otherwise equal conditions, caused a separation of flocks large enough to be kept back completely by a filter of a standard type. For colloidal solutions exhibiting anodic

convection under the influence of a current (arsenious sulphide and platinum), the precipitating power of a salt is practically independent of the anion, the valency of the cation being the determining factor. Tervalent ions are more effective than bivalent ions, and these again are more effective than univalent ones. For a colloidal solution of ferric hydroxide, which exhibits cathodic convection, the valency of the anion is the chief determining factor. Further, in the case of the univalent ions, an influence of the rate of migration may be detected; thus, in the precipitation of a colloidal solution exhibiting anodic convection, the acids are more effective than the salts yielding univalent cathions. Speaking generally, equivalent solutions of equally dissociated electrolytes, yielding ions of the same valency and with nearly equal rates of migration, are equally effective in the precipitation of colloidal solutions.

It has been shown that the precipitating effect is dependent not only on the concentration of the precipitating salt, but also on the rate at which the latter is added to the colloidal solution. This leads the author to regard the process in question as one involving the element of time (as a process of diffusion); it cannot be explained by a displacement of the statical equilibrium. As a working hypothesis, the author supposes the colloidal substance to be semipermeable to the ions, the character of the semipermeability being closely bound up with the direction of the convection (anodic or cathodic).

J. C. P.

Determination of Molecular Weights. VII. ERNST BECKMANN (*Zeit. physikal. Chem.*, 1903, 44, 161—196).—I. Boiling point method. A few minor improvements are suggested on the apparatus previously described (*Abstr.*, 1902, ii, 303). The tube for the introduction of the vapour of the solvent (marked *D* in sketch, *loc. cit.*) is now fused in near the bottom of the boiling point tube instead of at the top; the greater part of this tube is consequently in the outside boiling vessel.

II. Freezing point method. The author has previously described a freezing point apparatus with electromagnetic stirrer (*Abstr.*, 1897, ii, 88, 362), and in the present paper some minor modifications of that apparatus are suggested, chiefly with the view of making it less expensive.

An apparatus is described in which liquid air is used as the cooling agent, the liquid air being introduced between an inner and an outer Dewar tube.

The author also replies at length to recent criticisms of his freezing point apparatus.

J. C. P.

Crystallisation of Sparingly Soluble Substances. AUGUST DE SCHULTEN (*Compt. rend.*, 1903, 136, 1444—1446).—When 10 grams of hydrated barium chloride are dissolved in a mixture of 3 litres of water with 300 c.c. of concentrated hydrochloric acid, and to this there is added, at the rate of 1 or 2 drops per minute, a solution of 2 grams of sulphuric acid in 2 litres of water, crystals of barium sulphate begin to form at the end of 24 hours, and after the lapse of

one month from 8 to 9 grains of crystals of an average length of 5 mm. are produced. These show more facets than crystalline barium sulphate obtained by other methods, and have a sp. gr. 4.499 at 15°.

By the application of this method of slow admixture by diffusion to solutions of appropriate materials, crystalline preparations of a large number of insoluble substances have been prepared, including aluminium hydroxide, bismuth phosphate and arsenate, celestine, anglesite, bobierite, &c.

T. A. H.

Formation of Complexes and some Physico-chemical Constants for Mercury-Halogen Compounds. MILES S. SHERRILL (*Zeit. physikal. Chem.*, 1903, 43, 705—740).—The tendency of the mercury haloids to form complexes is well known (compare Le Blanc and Noyes, *Abstr.*, 1891, 388; Richards and Archibald, *Abstr.*, 1902, ii, 384). The author contributes a detailed study of the mutual relations of mercuric cyanide, iodide, bromide, and chloride to the corresponding potassium salts as indicated by *E.M.F.*, solubility, freezing point, and partition experiments. The formation of complexes is established in all cases, and if the complex anion formed is represented as $(\text{HgX}_2)_m\text{X}'_n$, the experimental work indicates that for most concentrations $m=1$ and $n=2$. When the mercury salt is in excess, complexes may be formed containing relatively more mercury, especially in the case of the chloride and bromide. Solubility and freezing point experiments with the cyanide point to the existence of a complex in which $m=1$, $n=1$. In the case of the iodide, indication was obtained of a complex with $m=2$, $n=3$. The order of solubility of mercuric and mercurous haloids, as well as the relative equilibrium constants which express the tendency to the formation of complexes, are in accordance with Bodländer's rule (*Abstr.*, 1898, ii, 554), and Abegg and Bodländer's theory of electro-affinity (*Abstr.*, 1899, ii, 542).

J. C. P.

Rates of Reactions in Solutions containing Ferrous Sulphate, Potassium Iodide, and Chromic Acid. CLARA C. BENSON (*J. Physical Chem.*, 1903, 7, 356—388).—The results of the experiments by the author and by DeLury (this vol., ii, 200, 471) have led to the following conclusions: the rate of liberation of iodine in the absence of ferrous salts is approximately proportional to the concentration of the dichromate and to the square of that of the acid, and the relation to the concentration of the iodide is given by an expression $R = mC + nC^2$. The rate is accelerated by ferric salts. In the absence of iodide, the rate of oxidation of ferrous sulphate is proportional to the squares of the concentration of the ferrous salt and of the acid, and to the 1/4th—1/8th power of dichromate concentration. Ferric salt retards the action. In the presence of ferrous salts, the rate of liberation of iodine is proportional to the 1/3rd—1/6th power of the concentration of the dichromate, to the 4th power of that of the acid, and to the 1st power of the concentrations of the ferrous salt and of the iodide. The action is retarded by ferric salts. In the presence of iodide, the rate of oxidation of ferrous sulphate is proportional to the concentration of the dichromate and ferrous sulphate and to the 3rd

or 4th power of the concentration of the acid. Increase of iodide causes at first a decrease and later an increase of the rate. The author considers that the results are not in accord with the peroxide theory, which assumes the primary product of oxidation of the ferrous sulphate to be a peroxide, which then reacts with the iodide and the remaining ferrous salt. Better agreement is obtained if the iodide is assumed to take part in the reaction, and the two reactions are suggested as occurring together (1) between Cr_2O_7 , FeI , I , and 4H , and (2) between Cr_2O_7 , 2Fe , and 2H .
L. M. J.

Change in the Rate of Inversion with Temperature. CARL KULLGREN (*Zeit. physikal. Chem.*, 1903, 43, 701—704).—Whilst the rapid increase with temperature of the velocity of a reaction (often 10—15 per cent. per degree) cannot be explained on kinetic grounds, the author makes a calculation to show that this increase in the case of sugar inversion may be almost completely accounted for by the increase with temperature of the degrees of dissociation of water and sucrose. The change in the dissociation is known for water from Kohlrausch and Heydweiler's researches, for sucrose from Madsen's work (*Abstr.*, 1901, ii, 228. Compare Kullgren, *Abstr.*, 1902, ii, 647). J. C. P.

Application of the Phase Rule to the Distillation of Turpentine. MAURICE VÉZES (*Bull. Soc. chim.*, 1903, [iii], 29, 470—478).—Crude turpentine, essentially a solution of about 75 per cent. of colophony in about 25 per cent. of oil of turpentine, constitutes a divariant system, and the form of its vapour tension curve is conditioned by the composition of the solution. When water is added to liquefied turpentine in sufficient quantity to produce a second liquid layer, the system remains divariant, and the vapour tension curve lies between that of (a) a heterogeneous mixture of oil of turpentine and water and (b) that of water alone (since colophony is not volatile at the temperatures concerned). The boiling point of the mixture can therefore only vary between 95° and 100° , and the molecular composition of the vapour, and therefore of the distillate, at any stage as regards (a) oil of turpentine and (b) water, is proportional to the vapour pressures of these liquids at the particular boiling point.

When steam is passed into turpentine, the system becomes tri-variant, and the form of the vapour tension curve is conditioned by the simultaneous compositions of the vapour and liquid phases; its displacement being limited by (1) the vapour pressure curve of a heterogeneous mixture of water and turpentine, and (2) the vapour pressure curve of turpentine. The boiling point may therefore range between the temperatures 97° and 184° , and the composition of the distillate produced ranges from that stated in the preceding paragraph to oil of turpentine free from water.

Boiling points for the construction of these curves are given in the original, and it is pointed out that the distillation of turpentine after admixture with excess of water, as carried out in the Landes district,

gives the best yield of oil of turpentine at the lowest possible temperature.
T. A. H.

Conception of Independent Components. JOHANNES J. VAN LAAR (*Zeit. physikal. Chem.*, 1903, 43, 741—744).—In reference to the discussion between Wegscheider and Nernst (this vol., ii, 356), the author expresses himself in favour of the latter's views. J. C. P.

Theory of Valency and of Molecular Compounds. RICHARD ABEGG (*Chem. Centr.*, 1903, i, 1203—1204; from *Vidensk. Skrift. I. Math.-natur. Klasse*, 1902, No. 12, *Christiania*).—Experimentally there is no hard and fast line to be drawn between atomic and molecular compounds, and in suggesting a theoretical basis for the possibility of varying valency, the author endeavours to look at both classes from the same standpoint. He supposes that each element has two opposite kinds of valencies, 'normal' and 'contra-valencies.' The latter are never fewer than the former, and the sum of the two together is 8. The normal valencies are the stronger, positive in the case of metals, negative in the case of metalloids, whilst their numbers in the first 7 groups of the periodic system are respectively 1, 2, 3, 4, 3, 2, 1. The eighth group contains elements without normal valency, and with 8 contravalencies.

It is not necessary that an element should exhibit its maximum valency; the higher this is, the greater is the tendency for valencies to become latent; this is especially the case with contravalencies. The higher the atomic weight of an element, the more important is the part played by the contravalencies. Thus, of the 7 positive contravalencies of the halogens, those of iodine are most in evidence. That the negative contravalencies of the metals are less active than the positive contravalencies of the halogens is probably connected with the fact that the positive electrons are much more closely bound up with matter than the negative. The weakness of the metallic contravalencies is associated with the fact that the metals are monatomic, and the evident contravalencies of the metalloids are regarded as responsible for the constitution of their molecules. Complex cations are much more seldom met with than complex anions, and this is attributed to the relative weakness of the metallic contravalencies.

The author regards the physical and chemical properties of a solvent, especially its dissociative power, as associated with the contravalencies of its constituent elements. Molecular association in liquids may be similarly regarded.
J. C. P.

Inorganic Chemistry.

Hydrogen Peroxide of Crystallisation. RICHARD WILLSTÄTTER (*Ber.*, 1903, 36, 1828—1829).—Wiede (*Abstr.*, 1898, ii, 295; 1899, i, 319) first observed that hydrogen peroxide forms molecular compounds with salts, and our knowledge of such substances has since been extended by Tanatar and others.

When a solution of ammonium sulphate in 30 per cent. hydrogen peroxide is evaporated over sulphuric acid, transparent plates and prisms of the composition $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$ separate. The crystals smell of ozone, and when they are warmed gently under diminished pressure, a concentrated solution of hydrogen peroxide can be distilled off. The solution of the salt in water has a feebly acid reaction.

From sodium sulphate, transparent, octahedral crystals of the composition $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O} \cdot \frac{1}{2}\text{H}_2\text{O}_2$ were prepared.

Such salts can be substituted for persulphates and percarbonates in certain reactions; they can be used medicinally instead of aqueous solutions of hydrogen peroxide. They part with hydrogen peroxide in ether and in other indifferent organic solvents. A. McK.

Catalytic Decomposition of Hydrogen Peroxide. II. J. H. KASTLE and A. S. LOEVENHART (*Amer. Chem. J.*, 1903, 29, 563—588. Compare this vol., ii, 415).—A theoretical paper, in which the mode of action of hydrogen peroxide as an oxidising agent and its catalytic decomposition by various substances are discussed. Hydrogen peroxide can oxidise certain substances directly, without the intervention of a catalyser and without the evolution of oxygen. In certain oxidations by hydrogen peroxide, oxygen, on the other hand, is evolved, and in some cases, as in the oxidation of nitriles, the same quantity of oxygen leaves the system as molecular oxygen, as that which remains in it combined with the oxidation products. Certain oxidations are not effected by hydrogen peroxide alone, but a catalyser is necessary. Again, hydrogen peroxide sometimes appears to act like a reducing agent. Those substances which induce oxidations by means of hydrogen peroxide are also capable of effecting its catalytic decomposition under certain conditions. The theory propounded by the authors to account for all these phenomena is that the hydrogen peroxide tends to unite with the oxidisable substance to form an unstable compound which will part with its oxygen more readily than does hydrogen peroxide itself; this compound will therefore act as an oxygen carrier. This view is supported by the fact that such additive compounds have been isolated by Schöne, de Forcrand, and others. When sulphurous acid is oxidised by hydrogen peroxide, for example, the labile holoxide compound, $\text{H} \cdot \text{SO}_2(\text{O}_2)\text{H}$, is supposed to be first formed. The so-called reductions with hydrogen peroxide are probably oxidations in their initial phases, that is, complex oxidation products are first formed and these then decompose; for instance, the interaction of

silver oxide and hydrogen peroxide is represented by the equations, (1) $\text{Ag}_2\text{O} + 3\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{H}_4\text{Ag}_2\text{O}_6$, (2) $\text{H}_4\text{Ag}_2\text{O}_6 = 2\text{Ag} + 2\text{H}_2\text{O} + 2\text{O}_2$. Manganese peroxide and lead peroxide decompose hydrogen peroxide in alkaline solution, remaining themselves unchanged, that is, unstable holoxides and hydroholoxides are formed which then decompose into water, molecular oxygen, and original catalyser.

Normal holopermanganic acid is supposed by the authors to be formed by the action of hydrogen peroxide on permanganic acid, thus: $\text{Mn}_2\text{O}_7 + 2\text{H}_2\text{O} + 5\text{H}_2\text{O}_2 = \text{H}_4\text{Mn}_2\text{O}_{19}$; the decomposition of holopermanganic acid is a gradual one, H_2O_3 being the intermediate product.

The unstable holoxide derivatives may act in two ways. They may either effect the oxidation of certain reducing agents, which cannot be oxidised by hydrogen peroxide alone, or, if such reducing agents are not at hand, these holoxide derivatives may undergo decomposition themselves, yielding molecular oxygen, water, and the catalyser in its original form, or a stable oxidation product of the latter. The fact that both those processes occur simultaneously, and that a good oxygen carrier is generally a good catalyser, and *vice versa*, is of itself evidence that these two processes are causally related.

The rôle of catalase in the living cell is discussed. Catalase is a substance or mixture of substances with a tendency to combine with hydrogen peroxide to form a very unstable holoxide derivative.

A. McK.

Regularities in the Composition of Halogen Double Salts. FRITZ EPHRAIM (*Ber.*, 1903, 36, 1912—1914. Compare this vol., ii, 418).—A detailed reply to Grossmann's criticisms (this vol., ii, 476).

W. A. D.

Mixtures of Iodine and Sulphur. R. BOULOUCH (*Compt. rend.*, 1903, 136, 1577—1578).—The melting and solidification curve of a mixture of iodine and sulphur has been followed by the dilatometric process. If the temperature is marked off on the abscissæ-axis and the volumes taken as the ordinates, a curve is obtained which consists of four parts: below 65.5° , an almost straight line which rises with increasing temperature; at 65.5° , a line perpendicular to the temperature axis; from 65.5 to t° , a line which rises rapidly; and above t° , a line which is nearly parallel to the first. This shows that all the mixtures contain a certain quantity of a eutectic mixture which melts at 65.5° , and that the complete fusion does not take place until the temperature t° is reached.

The composition of the eutectic mixture is represented by 0.543 of sulphur and 0.457 of iodine.

No evidence could be found of the existence of any definite chemical compound, and no solid solution seems to take place. J. McC.

Production of Ozone by High Tension and High Frequency Spirals. H. GUILLEMINOT (*Compt. rend.*, 1903, 136, 1653—1655).—The author describes an apparatus for the production of ozone by the silent discharge in air. The resonator consists of spirals of copper

wire with 15 to 20 turns in one plane; these are placed opposite each other, and enclosed so that a current of air can be passed between them. The advantages claimed are (1) that the great influence of resonators on each other is used to intensify the field; (2) that between the two resonators there is a large surface for the silent discharge; and (3) a series of modulations is set up which is useful for the production of ozone.
J. McC.

Peroxides. SIMEON TANATAR (*Ber.*, 1903, 36, 1893—1897).—The author expresses a doubt whether there is a constitutional difference between the so-called "true" and "false" peroxides; the fact that some peroxides give hydrogen peroxide and others oxygen and water when decomposed by acids is considered to be due to the different thermal values involved, and not to structural differences. The formation of hydrogen peroxide from water involves 23 Cal., and in order for this to be produced the necessary energy must be provided by the heat of combination of the metal of the peroxide and the radicle of the acid. The following facts are put forward in support of this view. Barium peroxide, which is undoubtedly a "true" peroxide, if a salt of hydrogen peroxide, should, on hydrolysis, give this substance; but, instead, it is slowly decomposed by water at the ordinary temperature, giving oxygen. Strong acids, such as hydrochloric acid, decompose barium peroxide, forming hydrogen peroxide; but weaker acids, for example, phenol and nitrophenols, liberate oxygen. Aluminium chloride acts on barium peroxide suspended in water, giving aluminium hydroxide and barium chloride, and liberating oxygen; if, however, an excess of chloride is used, the action is simply that of hydrochloric acid on the peroxide, and a solution of hydrogen peroxide is obtained, little oxygen being evolved.
W. A. D.

Hydration and Hardening of some Sulphates. PAUL ROHLAND (*Zeit. anorg. Chem.*, 1903, 35, 201—204).—The author points out the connection which exists between the hydration and the hardening of sulphates. The phase rule indicates which salts are subject to simultaneous hydration and hardening; it is only those which possess a point at which four (or more) phases can exist in equilibrium, as, for example: hydrated salt, anhydrous salt, solution, vapour. This point lies near the transition point, and it is only below this point that hydration can take place. The velocity of hydration may be either increased or diminished by catalysers.

Efflorescence is also discussed.

J. McC.

Probable Atomic Weight of Tellurium and Atomic Weight Calculations in General. KARL SEUBERT (*Zeit. anorg. Chem.*, 1903, 35, 205—209).—A reply to K  thner (this vol., ii, 360).
J. McC.

Reduction of Nitric Oxide by Alkaline Pyrogallol. CARL OPPENHEIMER (*Ber.*, 1903, 36, 1744—1748).—When pure nitric oxide is enclosed over mercury and paper pellets saturated with an alkaline solution of pyrogallol are introduced, about 20 per cent. of the gas is absorbed, the pyrogallol becoming dark brown in colour. The absorbed

product gives the reaction for nitrites with iodide-zinc-starch paper and with *m*-phenylenediamine paper when acidified. The residual gas is nitrous oxide, the unabsorbed nitric oxide having been reduced quantitatively to it; nitrogen is not produced. C. H. D.

Solubility of Phosphorus. C. STICH (*Chem. Centr.*, 1903, i, 1291; from *Pharm. Zeit.*, 48, 343—344).—Saturated solutions of phosphorus in almond oil, oleic acid, paraffin, water, and officinal acetic acid have been found to contain 1.25, 1.06, 1.45, 0.0003, and 0.105 per cent. of phosphorus respectively. E. W. W.

Retention of Arsenic by Animal Charcoal. JOHN MARSHALL and LEON A. RYAN (*Amer. J. Pharm.*, 1903, 75, 251—253).—By passing a solution containing 0.4455 gram of arsenious oxide in 3000 c.c. of water through a filter containing 777.885 grams of dry animal charcoal, it was found that the latter retained 64.30 per cent. of the arsenious acid. In a second experiment, a solution of 3.3972 grams of arsenious oxide in 3000 c.c. of water was passed through 763.7 grams of undried animal charcoal, when 39.02 per cent. was retained. The time required for the filtration was 3 hours in the first experiment and 2 hours in the second. W. P. S.

[Interaction of] **Boric Acid, Potassium Fluoride, and Hydrofluoric Acid.** RICHARD ABEGG, C. J. J. FOX, and WALTER HERZ (*Zeit. anorg. Chem.*, 1903, 35, 129—147).—At 25°, boric acid distributes itself in the ratio 3.35:1 between water and amyl alcohol. The distribution was also determined between solutions of potassium fluoride and amyl alcohol, and from the results it can be calculated how much of the boric acid is fixed by the potassium fluoride. The simplest expression of the results is: $F' + 2H_3BO_3 \rightleftharpoons [B_2O_3, F'] + 3H_2O$, but the existence of a complex anion $[B_2O_3, F']$ is extremely doubtful.

Potassium fluoride normally depresses the freezing point of water, and the results show that the salt dissociates into K^+ and F^- , and not into $2K^+ + F_2^{2-}$. The freezing points of solutions containing potassium fluoride and boric acid were also determined. From the results, the amount of boric acid which remains free can be calculated, and the values obtained agree with those from the distribution experiments.

The effect of the addition of boric acid to solutions of potassium fluoride on the conductivity shows that in a 0.5*N* solution of potassium fluoride, when 0.5*N* boric acid is added, about 0.3*N* is fixed by the salt.

The conductivities of solutions of hydrofluoric acid and of hydrofluoric and boric acids were determined. Addition of boric acid greatly increases the conductivity of concentrated solutions of hydrofluoric acid, but diminishes that of dilute solutions. This indicates that the boric acid combines with several molecules of the hydrofluoric acid to form an acid which is highly dissociated, even in concentrated solution. The reaction is, therefore, very different from that between potassium fluoride and boric acid. The results of the determination of the depression of the freezing point of water caused by hydrogen fluoride prove that this acid is bimolecular and has the formula H_2F_2 . The

depression of the freezing point of water caused by the addition of boric and hydrofluoric acids is not independent of the time, and this proves that, besides the reaction which takes place instantaneously between these two substances, another slower action also takes place. This slower reaction was also proved by determining the titre of a mixed solution immediately after making up, and again after the lapse of some time. The titration was carried out with alkali, using phenolphthalein as indicator, and again after mannitol was added, so that both the "strong" acid and the free boric acid were determined. The initial titre is much higher than the end titre, and apparently 4 to 5 mols. of hydrofluoric acid combine with 1 mol. of boric acid. The slow reaction is irreversible. From these titration results, an attempt has been made to calculate the order of the reaction. The reaction in dilute solution is possibly bimolecular, but as the concentration increases the reaction becomes one of a higher order. Various possible reactions are discussed, but only the two represented by the equations $2\text{H}_2\text{F}_2 + \text{H}_3\text{BO}_3 = 1$ mol. of a monobasic acid (HBF_4), and $2\text{H}_2\text{F}_2 + \text{H}_3\text{BO}_3 = 1$ mol. of a dibasic acid, seem probable.

A mixture of the two acids was kept at 26° for several days in a platinum flask, then sodium hydroxide was added until the "strong" acid was neutralised. The free boric acid was then extracted with amyl alcohol, and, on evaporating the solution at the ordinary temperature in a vacuum, tabular crystals of a sodium salt separated. At a temperature higher than 300° , these lose water and boric acid; they contain about 25 to 26 per cent. of sodium, and it is not possible to bring this result into agreement with either of the two equations just given.

The solubility of boric acid in hydrofluoric acid was determined.

The second reaction between potassium fluoride and boric acid is very much slower than that with hydrofluoric acid, but, nevertheless, it takes place, as was proved by determining the freezing point of a solution containing potassium fluoride and boric acid before and after boiling. After boiling, the depression was smaller, showing that fewer dissolved molecules were present.

It has not yet been found possible to give a satisfactory chemical explanation of the results recorded. J. McC.

Silicon Amide and Imide. ÉMILE VIGOUROUX and CHARLES HUGOT (*Compt. rend.*, 1903, 136, 1670—1672).—Ammonia and silicon tetrachloride were liquefied in the limbs of a tube having the form of H, the cross-piece being provided with a stop-cock. The stop-cock was opened and the substances were allowed to react. When the temperature is kept throughout below 0° , *siliconamide* is formed: $\text{SiCl}_4 + 8\text{NH}_3 = \text{Si}(\text{NH}_2)_4 + 4\text{NH}_4\text{Cl}$. It is an amorphous, white powder, which is only stable below 0° , is insoluble in liquid ammonia, and is decomposed by water: $\text{Si}(\text{NH}_2)_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 4\text{NH}_3$. When the amide is heated above 0° , decomposition occurs and *siliconimide* is formed: $\text{Si}(\text{NH}_2)_4 = 2\text{NH}_3 + \text{Si}(\text{NH})_2$. The decomposition is complete at 120° , and takes place more readily under diminished pressure. The imide is amorphous and very stable, not being decomposed by heating in a vacuum to the temperature at which glass begins to soften. It

does not react with ammonia under any conditions to reproduce the amide, but is decomposed by water : $\text{Si}(\text{NH})_2 + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{NH}_3$.
J. McC.

Silicates. II. Action of Hydroxides of the Alkaline-earth Metals on Silicic Acid with less than 23 per cent. of Water. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1903, 35, 148—153. Compare this vol., ii, 475).—The following barium and strontium silicates have been obtained from various specimens of silicic acid :

Percentage of water in the silicic acid.	Percentage concentration of		Silicate produced.	
	Ba(OH) ₂	Sr(OH) ₂		
36·01	3·5	—	BaSiO ₃ , H ₂ O	—
—	1·06	0·75	(BaO) ₂ (SiO ₂) ₃ , 2·6H ₂ O	(SrO) ₂ (SiO ₂) ₆ , 5H ₂ O
21·9	3·5	—	(BaO) ₂ (SiO ₂) ₄ , 3H ₂ O	—
—	—	1·75	—	(SrO)(SiO ₂) ₄ , 2H ₂ O (?)
16·5	3·5	—	(BaO) ₃ (SiO ₂) ₄ , 4·6H ₂ O	—
—	—	1·75	—	(SrO) ₄ (SiO ₂) ₃ , 4·6H ₂ O
9·5	3·5	—	(BaO) ₃ (SiO ₂) ₄ , 5H ₂ O	—
—	3·5	—	BaSiO ₃ , H ₂ O	—
—	1·26	0·89	BaSiO ₃ , H ₂ O	(SrO) ₃ (SiO ₂) ₆ , 5H ₂ O
0·0	3·5	—	(BaO)(SiO ₂) ₉ , H ₂ O	—
—	3·5	—	(BaO) ₅ (SiO ₂) ₅₉ , 7H ₂ O	—
—	1·08	0·77	BaO(SiO ₂) ₃ , H ₂ O	(SrO) ₄ (SiO ₂) ₁₁₁ , 5H ₂ O
—	—	—	—	(SrO) ₄ (SiO ₂) ₂₀ , 3H ₂ O
—	—	—	—	(SrO) ₃ (SiO ₂) ₆ , 5H ₂ O
—	2·46	1·75	(BaO) ₄ (SiO ₂) ₁₅ , 4H ₂ O	(SrO) ₂ (SiO ₂) ₅₇ , 7H ₂ O

Some of these silicates are quite homogeneous and well crystallised, whilst the crystalline structure of others can be recognised by the polarisation microscope. The individuality of some of them is doubtful.

It is noticeable that the barium silicates contain about 10 per cent. of water, and the strontium silicates about 15 per cent. J. McC.

Silicic Acid and Silicates of the Alkalis and Alkaline Earths. E. H. KANTER (*Bull. Soc. chim.*, 1903, [iii], 29, 478—481. Compare Jordis and Kanter, this vol., ii, 364, 475, and preceding abstract).

T. A. H.

Proportion of Argon in the Vapour Rising from Liquid Air. LORD RAYLEIGH (*Phil. Mag.*, 1903, [vi], 5, 677—680).—When the boiling points of oxygen, argon, and nitrogen are taken into account, it is to be expected that any process of evaporation and condensation leading to an increase of the oxygen relatively to the nitrogen will also lead to an increase of the argon relatively to the nitrogen, and to a decrease of the argon relatively to the oxygen. This was borne out by the experiments described in this paper. With a rise in the percentage of oxygen from 30 to 90, the percentage of argon in the

vapour remained practically constant (1.3—2); expressed, however, as a percentage of nitrogen + argon, the argon increased from 1.9—20.
J. C. P.

Behaviour of Phenolphthalein towards Neutral and Acid Carbonates of the Alkalis. M. GIRAUD (*Bull. Soc. chim.*, 1903, [iii], 29, 594).—It is shown that the acid carbonates of the alkalis are neutral to phenolphthalein, and the normal carbonates alkaline.

T. A. H.

Action of Hydrogen Peroxide on Sodium Thiosulphate. RICHARD WILLSTÄTTER (*Ber.*, 1903, 36, 1831—1833).—Hydrogen peroxide acts on sodium thiosulphate according to the equation $2\text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O}_2 = \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$. On the gradual addition of hydrogen peroxide to an aqueous solution of sodium thiosulphate, the solution becomes alkaline and finally neutral; the changes represented by the equations (a) $3\text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O}_2 = 2\text{Na}_2\text{S}_3\text{O}_6 + 2\text{NaOH} + 3\text{H}_2\text{O}$, (b) $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} + 4\text{H}_2\text{O}_2 = 2\text{Na}_2\text{SO}_4 + 5\text{H}_2\text{O}$, probably take place. When concentrated solutions are employed, the reaction is violent.

The reaction affords a very convenient method for the preparation of sodium trithionate, $\text{Na}_2\text{S}_3\text{O}_6 \cdot 3\text{H}_2\text{O}$, which crystallises in transparent plates very easily soluble in water. The salt is identical with that prepared by Villiers (*Abstr.*, 1888, 915) by the action of sulphurous acid on sodium thiosulphate.

The author's experiments are at variance with those of Nabl (*Abstr.*, 1901, ii, 16, 94).
A. McK.

So-called Colloidal Silver. MAURICE HANRIOT (*Compt. rend.* 1903, 136, 1448—1449. Compare *Abstr.*, 1902, ii, 500, and this vol., ii, 368).—When "collargol" is purified by repeated precipitation from its solutions in ammonia by addition of dilute acetic acid, lysalbic acid (*Abstr.*, 1902, i, 653) remains in the mother liquors, and the product acquires a constant composition corresponding with that of a combination of 6.1 per cent. of lysalbin with 93.1 per cent. of silver. When heated under reduced pressure, small quantities of hydrogen and of carbon dioxide are evolved.

Colloidal silver, prepared by Schneider's modification of Carey Lea's method, contained 89.3 per cent. of silver, and could not be obtained free from iron, sulphuric acid, and organic matter. It is less stable than "collargol," and differs from the latter in its behaviour towards ammonia and acetic acid (compare Chassevant and Posternak, this vol., ii, 478), but like it furnishes small quantities of hydrogen and carbon dioxide when heated under reduced pressure. T. A. H.

Influence of Copper in the Silvering of Glass. LÉO VIGNON (*Bull. Soc. chim.*, 1903, [iii], 29, 515—517).—It is shown that the presence of small quantities of copper (such as occur in water distilled from copper vessels) or of copper salts materially influences the character and the temperature of formation of silver mirrors,

produced by the reduction of silver tartrate dissolved in dilute ammonia, upon glass. In the absence of copper, no deposition of silver occurs until the temperature reaches 80° , and then a very white mirror is formed; in the presence of 0.00005 per cent. of copper, a similar mirror is deposited at 30° ; with 0.0001 per cent. of copper, a somewhat red mirror is produced at 30° , a yellow one at 40° , and a dull black deposit at 50° ; with larger amounts of copper, black deposits are formed even at 30° .
T. A. H.

Fusibility of Mixtures of Antimony and Silver Sulphides.
H. PÉLABON (*Compt. rend.*, 1903, 136, 1450—1452).—The fusibility curve of mixtures of sulphides of antimony and silver, obtained by plotting as ordinates solidification temperatures, determined from cooling curves, against the percentage compositions in silver sulphide of the corresponding mixtures as abscissæ, shows six straight portions, two of which are joined by curves.

This indicates the existence of two compounds having the formulæ $\text{Sb}_2\text{S}_3, \text{Ag}_2\text{S}$ (m. p. 503°) and $\text{Sb}_2\text{S}_3, 3\text{Ag}_2\text{S}$, and of three eutectic mixtures containing 17.5, 52.7, and 79 per cent. of silver sulphide, and melting at 438° , 440° , and 454° respectively.
T. A. H.

Argentammonium Bases and Silver Hydrocyanic Acid.
HANS EULER (*Ber.*, 1903, 36, 1854—1860).—A series of physical measurements on solutions of moist silver oxide in ammonia. Similar measurements have been made by Bodländer and Fittig (*Abstr.*, 1902, ii, 248) on the salts of this base. Conductivity determinations in a silver nitrate solution containing ammonia showed that it hardly differs from silver nitrate alone, accordingly the ion $\text{Ag}(\text{NH}_3)_2$ has the same velocity as the Ag ion. The solution of silver oxide in ammonia scarcely lowers the freezing point, showing that the number of dissolved molecules is hardly altered. These facts, together with measurements of *E.M.F.* in the concentration cell: silver | silver oxide in ammonia solution | dilute silver nitrate | silver, in which the concentration of silver oxide and ammonia varied, proved the cathion present in solution to be $\text{Ag}(\text{NH}_3)_2$. From this, the concentration of the silver ions is known, and the constant

$$K = [\text{Ag}][\text{NH}_3]_2 / [\text{Ag}(\text{NH}_3)_2]$$

(where [] denotes the respective concentration) was calculated to be 4.9×10^{-8} .

Solubility determinations of the solubility of silver oxide by Noyes and Kohr give the value 7.0×10^{-8} for K , whilst Bodländer and Fittig found 7.9×10^{-8} electrically and 5.66×10^{-8} by solubility determinations. These give a mean of 6.35×10^{-8} for K .

Similar measurements with methylamine gave a value of 2.45×10^{-7} for K , which signifies that the methylamine base is five times less stable than the ammonia base.

Hydrocyanic acid dissolves silver cyanide to form the very strong silver-hydrocyanic acid, which crystallises in needles and is dissociated into the ions $\text{Ag}(\text{CN})_2$ and H.
E. F. A.

The Second Anhydrous Modification of Calcium Sulphate. PAUL ROHLAND (*Zeit. anorg. Chem.*, 1903, 35, 194—200).—In view of the fact that the statements in text-books concerning calcium sulphate are frequently erroneous, the author gives a *résumé* of the transition temperatures of the hydrates. The transition temperature of the semihydrate into the second anhydrous modification (hydraulic or Estrich gypsum) is 525° .

The influence of various salt solutions on the hardening of this second anhydrous modification of calcium sulphate has been studied, and the results obtained are compared with those previously found (*Zeit. Baumaterialienkunde*, 1901, 6, 19, 22) for the semihydrate. Ammonium, calcium, magnesium, and aluminium chlorides, potassium chromate, and borax accelerate the hardening, whilst sodium chloride, potassium and aluminium sulphates, and potassium nitrate retard it. The influence of these salts on the hardening is not the same in all cases, either in degree or in direction, as on the hardening of the semihydrate. The catalytic influence of these electrolytes is to be found in the different solution pressures of the anhydride in the solutions.

The author discusses the process of hardening in its connection with solubility and velocity of hydration. J. McC.

The Melting Point of Calcium Silicate (CaSiO_3), Sodium Silicate (Na_2SiO_3), and of their Mixtures. N. V. KULTASCHEFF (*Zeit. anorg. Chem.*, 1903, 35, 187—193).—The melting point of sodium silicate and a series of mixtures of this with calcium silicate was determined by means of a Le Chatelier thermo-element. The melting point of sodium silicate is 1007° , and that of calcium silicate is above 1400° . The melting point curve shows changes of direction when the mixture contains 80 per cent. of sodium silicate (minimum), 60 per cent. of sodium silicate, 40 per cent. of sodium silicate (maximum), and 20 per cent. of sodium silicate (minimum). The mixtures were prepared by fusing the requisite amounts of sodium carbonate, silica, and calcium oxide together. If any excess of silica is used, the mass solidifies to a glass, and no definite melting point could be observed.

The mixture of maximum melting point (1160°) has very nearly the composition $2\text{Na}_2\text{SiO}_3 \cdot 3\text{CaSiO}_3$, and must be considered a true chemical compound. It could be isolated in homogeneous, monoclinic, twin crystals. When the mixture contains 60 to 80 per cent. of calcium silicate, mixed crystals of this compound and calcium silicate separate. When the mixture contains 40 to 60 per cent. of calcium silicate, mixed crystals of the compound $3\text{Na}_2\text{SiO}_3 \cdot 2\text{CaSiO}_3$ and the other compound are deposited. From a mixture containing 30 to 35 per cent. of calcium silicate, a solid is obtained which, on boiling with water, leaves an insoluble residue of the compound $3\text{Na}_2\text{SiO}_3 \cdot 2\text{CaSiO}_3$.

The influence on the melting point of the addition of a slight excess of silica was also determined. The addition of silica to sodium silicate lowers the melting point, but a small addition to mixtures

of the two silicates either does not alter the melting point or slightly raises it, but further addition then depresses the melting point. It must therefore be assumed that in the mixtures rich in calcium silicate the silica dissolves in the crystallised compound $3\text{Na}_2\text{SiO}_3, 2\text{CaSiO}_3$.

J. McC.

Strontium Ferrate. WILHELM EIDMANN and L. MOESER (*Ber.*, 1903, 36, 2290—2291).—Strontium ferrate was precipitated by the addition of strontium bromide to an aqueous solution of potassium ferrate. Like the barium salt, it is a dark red, amorphous powder, sparingly soluble in water, and readily decomposable with evolution of oxygen and formation of ferric and strontium hydroxides. It is insoluble in alcohol and in ether.

A. McK.

Action of some Gases on Barium Ammonium. ANTOINE GUNTZ and MENTREL (*Bull. Soc. chim.*, 1903, [iii], 29, 585—587).—When barium ammonium, dissolved in liquefied ammonia, is treated at -50° with dry oxygen, the latter is absorbed with the formation of a white, gelatinous precipitate of indefinite composition, which, when dissolved in hydrochloric acid, is decomposed with the formation of ammonia and hydrogen peroxide. Carbon monoxide, under the same conditions, produces *barium carbonyl*, $\text{Ba}(\text{CO})_2$, a yellow powder, which is unstable in air, becomes brown at 100° , and incandescent at 250° , forming barium oxide and carbonate and carbon. Carbon monoxide reacts with metallic barium at 500° , producing a superficial layer of barium carbide.

With barium ammonium, dissolved in liquefied ammonia, nitrogen dioxide furnishes a gelatinous precipitate of barium hyponitrite, which is decomposed by water with the evolution of nitrogen monoxide. Barium ammonium may also be obtained by the solution of barium amalgam (60 per cent.) in liquefied ammonia.

T. A. H.

Bariumamide and Barium Nitride. ANTOINE GUNTZ and MENTREL (*Bull. Soc. chim.*, 1903, [iii], 29, 578—585. Compare this vol., ii, 410).—When barium, contained in nickel or iron vessels, is heated in a current of dry ammonia at 200° , bariumamide, $\text{Ba}(\text{NH}_2)_2$, is produced as a greyish-white mass, which blackens and liquefies at 280° , becomes green at 340° , resolidifies at 280 — 275° , and is decomposed by moist air with the evolution of ammonia. When heated at 460° in a current of dry ammonia, it is partially decomposed with the formation of barium nitride, Ba_3N_2 ; the latter may be obtained alone by heating the bariumamide in a vacuum at 430° (compare Maquenne, *Abstr.*, 1892, 776). The nitride is a voluminous, homogeneous, yellow powder, which volatilises slightly at 1000° , but does not melt; it is decomposed by water into ammonia and barium hydroxide, and when heated at 400° in dry ammonia is partially reconverted into bariumamide.

T. A. H.

Combustion of Magnesium. ANASTASIOS K. CHRISTOMANOS (*Ber.*, 1903, 36, 2076—2082).—In burning a metre of magnesium ribbon 2.5 mm. wide, 83 per cent. of the oxide was driven off in smoke

whilst with ribbon 6 mm. wide the proportion disseminated was only 70 per cent. When burnt in contact with a cold piece of glass, the loss was reduced to 31 per cent.; the deposit on the glass is dark in colour and appears to contain 22 per cent. of unburnt metal, and on burning magnesium ribbon in air a dark zone of metallic vapour can be seen between the metal and the incandescent oxide; the ash can only be rendered colourless by long continued heating in air.

T. M. L.

Etching Fluid for Micro-metallurgy. WILLIAM RAMSAY (*Chem. News*, 1903, 87, 291).—In demonstrating the micro-structure of copper alloys, use is made of ammonia; the reaction, however, largely depends on the absorption of atmospheric oxygen and is somewhat irregular. By using somewhat dilute ammonia and gradually adding hydrogen peroxide, more satisfactory results are obtained.

L. DE K.

Action of Arsenic on Copper. ALBERT GRANGER (*Compt. rend.*, 1903, 136, 1397—1399).—When carbon dioxide mixed with arsenic vapour is conducted over finely-divided copper heated to the boiling point of sulphur, *copper arsenide*, Cu_3As_2 , is obtained. It forms regular crystals with a metallic lustre, has a sp. gr. 7.56, and is soluble in nitric acid. It is easily attacked by chlorine and bromine and tarnishes in the air.

At a higher temperature, crystals of copper arsenide, Cu_3As , are formed. Both of these arsenides decompose when strongly heated.

The arsenide, Cu_3As_2 , can be prepared by the action of arsenious chloride on copper or of arsenic on cuprous chloride.

The corresponding *copper phosphide*, Cu_3P_2 , is formed when carbon dioxide containing phosphorus vapour is conducted over copper at a red heat. At a lower temperature, the phosphide, Cu_2P , is produced.

J. McC.

Mercuric Chloride and Water. DANIEL STRÖMHOLM (*Zeit. physikal. Chem.*, 1903, 44, 63—73. Compare this vol., i, 138).—Comparison of the solubility of mercuric chloride in dry ether and in ether containing varying quantities of water leads to the conclusion that mercuric chloride and water are combined as hydrate in ethereal solution. On the hypothesis that a monohydrate is formed, the equilibrium coefficient for the reaction $\text{HgCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HgCl}_2 \cdot \text{H}_2\text{O}$ is found to be approximately constant within certain limits of concentration. On the whole, however, there is evidence that higher hydrates also exist.

The paper contains supplementary remarks relative to the author's previous work (*loc. cit.*).

J. C. P.

Preparation of Crystalline Sodium Alum. GUSTAVE DUMONT (D.R.-P. 141670).—Crystalline, non-efflorescent sodium alum may be prepared by mixing neutral solutions of aluminium and sodium sulphate, concentrating to sp. gr. 1.38—1.42, and allowing to cool. The amorphous mass formed at first changes into stable, non-efflorescent

crystals in the course of a few days. Hitherto, acid solutions have been employed, and a non-efflorescent product has not been obtained.

C. H. D.

Indium Oxide. CARL RENZ (*Ber.*, 1903, 36, 1847—1850).—Indium oxide retains its straw-yellow colour even when purified by precipitation as sulphite until all traces of iron are removed. When heated very strongly on iridium foil, it becomes grey, and is then only partly soluble in dilute acids. The white, amorphous residue is quite insoluble in hot concentrated acids. When treated with excess of ammonia, the acid filtrate yields a precipitate of unaltered yellow oxide. Some oxide goes into solution; this is precipitated on neutralising with acid as a white hydroxide, which, on drying, forms a greyish-white, amorphous oxide. These three polymeric forms of the oxide show identical spectra.

When heated in the oxyhydrogen flame, rods of indium oxide remained unmelted long after similar rods of aluminium oxide had melted. In one experiment, after removing the flame, the surface of the oxide was found to be covered with minute, crystalline splinters, which probably represent a crystalline form of the oxide.

E. F. A.

Mode of Oxidation of Manganese Salts by Alkali Persulphates in Acid Solution. HENRI BAUBIGNY (*Compt. rend.*, 1903, 136, 1662—1664. Compare this vol., ii, 512).—The precipitation of manganese dioxide from an acid solution of a manganous salt by potassium permanganate depends on the acidity, on the concentration of the salts, and on the temperature. The presence of the acid retards the precipitation and may even completely prevent it. The amount of manganic salt which remains dissolved increases with the concentration of the acid, but diminishes as the temperature rises. The precipitate consists solely of manganese dioxide and contains no manganic oxide.

When manganous salts are oxidised in acid solution with a persulphate, a manganic salt is formed either directly or secondarily from the permanganic acid produced. The manganic salt is then decomposed with formation of manganese dioxide, but as the concentration of the acid present increases, more of this salt remains undecomposed.

J. McC.

Theory of Nickel Steels. CHARLES E. GUILLAUME (*Compt. rend.*, 1903, 136, 1638—1641).—According to the amount of nickel present, alloys of iron and nickel may show thermal hysteresis or not. Since the alloys are quite analogous in other properties, the conclusion is drawn that the thermal hysteresis is of a secondary character. The expansion by heat of nickel steels corresponds with the expansion of iron, and probably, therefore, the alloy undergoes transformations just as iron passes from the γ - to the β - and from the β - to the α -conditions at definite temperatures.

The phenomena can be explained by assuming that the reversible nickel steels are solutions of iron in nickel and of nickel in iron which

tend to pass into a state of equilibrium conditioned by the proportions of α - and γ -iron corresponding with each temperature.

J. McC.

Forms of Silicon in Iron. THEODOR NASKE (*Chem. Zeit.*, 1903, 27, 481—484).—Dilute sulphuric acid dissolves completely alloys of iron and silicon, which contain only small quantities of manganese, but in the case of alloys containing from 15 to 18 per cent. of manganese leaves undissolved a small residue having a constant composition $(\text{Fe}, \text{Mn})_3\text{Si}$. In a similar manner, dilute nitric acid fails to leave undissolved residues corresponding with definite compounds of iron and silicon, but in the case of alloys containing more than 10 per cent. of silicon, an ammoniacal solution of cupric chloride gives magnetic residues, which had the composition Fe_3Si or $(\text{Fe}, \text{Mn})_3\text{Si}$. An alloy containing 51 per cent. of silicon, when treated with dilute hydrofluoric acid in aqueous potassium hydroxide, is only partially dissolved, and a grey, non-magnetic, finely-crystalline residue is left consisting of Fe_3Si ; the same alloy contains, in addition to this compound, a substance which is decomposed by the solvents, giving silicon tetrafluoride and soluble silicic acid. An alloy containing 80.44 per cent. of silicon gives, under similar conditions, small leaflets similar to graphite, having a metallic lustre and consisting of nearly pure silicon.

When iron containing from 5—12 per cent. of silicon is gently warmed with an excess of sulphur, very vigorous interaction occurs and the mass becomes incandescent; on powdering the product, it can be resolved into a magnetic and non-magnetic portion, the former predominating. Analyses of magnetic portions from various alloys were found to correspond with definite compositions, $\text{Fe}_3\text{Si}, 8\text{FeS}$; $\text{Fe}_3\text{Si}, 3\text{FeS}$; $\text{Fe}_3\text{Si}, 2\text{FeS}$, and $\text{Fe}_3\text{Si}, \text{FeS}$, and when manganese is present to the extent of 10—20 per cent., the whole of the product is magnetic and has the composition $(\text{Fe}, \text{Mn})_3\text{Si}, (\text{Fe}, \text{Mn})\text{S}$.

From these facts, the author concludes that in ordinary cast iron the silicon is present as the silicide, Fe_3Si , and that when an excess of iron is present, this compound separates in a crystalline form with a number of atoms of "iron of crystallisation." An excess of silicon separates always in the elementary form. Alloys containing a high percentage of silicon can only be prepared in an electric furnace, and in these the silicon is present as Fe_2Si , FeSi_2 , or FeSi_3 , according to the composition of the alloy and the temperature of its formation.

W. A. D.

Pentamminenitrosocobalt Salts. JULIUS SAND and OTTO GEUSSLER (*Ber.*, 1903, 36, 2083—2086).—By passing pure nitric oxide into a solution of a cobaltous salt saturated with ammonia, two series of isomeric compounds are produced.

I. *Black Series*.—The compound, $\text{Co}(\text{NH}_3)_5\text{NOCl}_2$ or $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}\text{Cl}_4$, forms black, glistening crystals, and when covered with water or dilute acids liberates nitric oxide, just as the oxygen compound (this vol., i, 467) liberates oxygen.

II. *Red Series*.—The nitrate, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{NO}_3)_4, \text{H}_2\text{O}$, forms

red crystals which can be recrystallised unchanged from water. The double *nitrate*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{NO}_3)_4$, AgNO_3 , forms brownish-yellow, pointed needles. The *acid nitrate*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{NO}_3)_4, 2\text{HNO}_3$, forms a red, shimmering precipitate and is regarded as an oxonium salt. The *perchlorate*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{ClO}_4)_4, 2\text{HNO}_3$, prepared by the action of perchloric acid on the first compound of the series, is a pale red precipitate; similar precipitates are formed by chloroplatinic acid, potassium ferrocyanide, potassium dichromate, and picric acid, but not by hydrochloric acid or ammonium oxalate.

The *sulphate*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{SO}_4)_2, \text{H}_2\text{O}$, is a red, crystalline precipitate, and gives a quantitative yield of nitrous oxide with concentrated sulphuric acid. The *anhydrous* sulphate is formed when the hydrate is left in a vacuum over sulphuric acid. The *nitrate*, $\text{Co}_2(\text{N}_2\text{O}_2)(\text{NH}_3)_{10}(\text{NO}_3)_4, \text{H}_2\text{SO}_4$, is precipitated in the form of spangles by the action of nitric acid on the sulphate; perchloric acid gives a similar precipitate.

T. M. L.

Chromates of Polyvalent Metals. OTTO MAYER (*Ber.*, 1903, 36, 1740—1743).—The dark red and iodine-like crystals of silver dichromate (compare Antenrieth, *Abstr.*, 1902, ii, 457) dissolve in 12,000 parts of cold water. They are not altered by boiling with nitric acid, no trichromate being formed. For quantitative analysis, the salt is dissolved in dilute ammonia, the excess of ammonia removed by boiling, and the silver precipitated as chloride. The filtrate is evaporated to dryness with hydrochloric acid and alcohol, and the residue ignited to chromic oxide.

Lead dichromate, PbCr_2O_7 , prepared by heating lead acetate with chromium trioxide in concentrated nitric acid for several hours in a reflux apparatus, forms small, reddish-brown crystals which exhibit pleochroism. When lead chloride is added to a boiling solution of chromic acid, small, red, prismatic needles separate on cooling, which consist of equal molecules of lead chromate and dichromate.

C. H. D.

Titanium Tetrafluoride. OTTO RUFF and RICHARD IPSEN (*Ber.*, 1903, 36, 1777—1783).—Titanium tetrafluoride cannot be prepared by roasting the acid H_2TiF_6 with sulphuric acid or by distilling titanous acid with calcium fluoride and sulphuric acid. It can be prepared (1) by the action of fluorine on titanium, (2) by the action of anhydrous hydrogen fluoride (from potassium hydrogen fluoride) on titanium (the hydrogen fluoride prepared from calcium fluoride and sulphuric acid gives only oxyfluorides), (3) by passing dry hydrogen fluoride over titanium tetrachloride at 100—120°. *Titanium tetrafluoride* is a colourless mass which melts and sublimes above 400° to a hard, transparent mass; its high melting and boiling points distinguish it sharply from the fluorides of the metalloids, which boil at a lower temperature than the chlorides (titanium tetrachloride boils at 136°; the tetrabromide at 230°), and place it with the fluorides of the metals. It is very hygroscopic and dissolves in water to a clear liquid which, on evaporation, deposits the *hydrate*, $\text{TiF}_4, 2\text{H}_2\text{O}$. The *alcoholate*, $\text{TiF}_4, \text{C}_2\text{H}_6\text{O}$, is not completely crystalline. Dry ammonia gives the compound $\text{TiF}_4, 2\text{NH}_3$, which

sublimes without decomposition and dissolves in water to a clear solution which slowly deposits titanitic acid when boiled. The *pyridine* compound, $\text{TiF}_4 \cdot \text{C}_5\text{H}_5\text{N}$, is a white, crystalline substance. The tetrafluoride does not combine directly with hydrogen fluoride, but is completely converted into the dioxide by roasting with sulphuric acid. Sodium and magnesium, and iron, aluminium, and boron at a red heat reduce it to titanium; copper and silicon reduce it only to the hexafluoride. The fluoride dissolves unchanged in cold phosphorus oxychloride, but at 30° a vigorous action takes place and the chloride and phosphorus oxyfluoride are produced; excess of phosphorus oxychloride gives a quantitative yield of the yellow *compound*, $\text{TiCl}_4 \cdot 2\text{POCl}_3$, which melts at 107° and boils at 138° .
T. M. L.

Compounds of Quadrivalent Vanadium. IWAN KOPPEL and E. C. BEHRENDT (*Zeit. anorg. Chem.*, 1903, 35, 154—186. Compare Abstr., 1902, ii, 87).—For the reduction from quinquevalent to quadrivalent vanadium, hydroxylamine hydrochloride, dextrose, formaldehyde, alcohol, oxalic acid, sulphur dioxide, or hydrogen sulphide may be used. The best results are obtained with sulphur dioxide. It has been found that vanadyl sulphate separates from solutions which contain up to three molecules of sulphuric acid per molecule of vanadium pentoxide reduced. If more sulphuric acid is present, an acid salt separates. The following vanadyl sulphates have been obtained: $\text{VOSO}_4 \cdot 6.5\text{H}_2\text{O}$; $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$; $\text{VOSO}_4 \cdot 3.5\text{H}_2\text{O}$; $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$; and VOSO_4 ; and the following acid salts: $(\text{VO})_2\text{H}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$; $(\text{VO})_2\text{H}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$; $(\text{VO})_2\text{H}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$; and the anhydrous salt $(\text{VO}_2)_2(\text{SO}_3)_3$. The results obtained are in agreement with those found by Gerland (*Ber.*, 1876, 9, 869; 1877, 10, 2111).

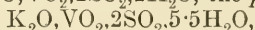
By reducing a metavanadate dissolved in dilute sulphuric acid with sulphur dioxide, then adding excess of alkali sulphate and evaporating at a higher temperature, a light blue, crystalline powder of $\text{R}_2\text{SO}_4 \cdot 2\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ is obtained. In this way, *ammonium divanadyl sulphate*, $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{VOSO}_4 \cdot \text{H}_2\text{O}$, has been obtained, which loses its water of crystallisation at 175° . The *sodium* salt, $\text{Na}_2\text{SO}_4 \cdot 2\text{VOSO}_4 \cdot 2.5\text{H}_2\text{O}$, and the *potassium* salt, $\text{K}_2\text{SO}_4 \cdot 2\text{VOSO}_4$, were also prepared. The conductivities of these salts have been determined.

When to a neutral solution of these salts alcohol is added, a heavy, deep blue oil is precipitated and a light blue, flocculent precipitate is formed in the upper layer. In contact with alcohol, the oil solidifies in 7 or 8 days, and the solid has the composition $\text{R}_2\text{SO}_4 \cdot \text{VOSO}_4 \cdot x\text{H}_2\text{O}$. The *ammonium* salt, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{VOSO}_4 \cdot 3.5\text{H}_2\text{O}$, the *sodium* salt, $\text{Na}_2\text{SO}_4 \cdot \text{VOSO}_4 \cdot 4\text{H}_2\text{O}$, and the *potassium* salt, $\text{K}_2\text{SO}_4 \cdot \text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, have been prepared.

When 1 mol. of ammonia is mixed with a solution of 1 mol. of a metavanadate and the whole reduced with sulphur dioxide and evaporated on the water-bath in a current of sulphur dioxide, a series of *blue* alkali vanadyl sulphites, $\text{R}_2\text{O} \cdot 3\text{VO}_2 \cdot 2\text{SO}_2 \cdot x\text{H}_2\text{O}$, is produced. The *ammonium* salt, $(\text{NH}_4)_2\text{O} \cdot 3\text{VO}_2 \cdot 2\text{SO}_2 \cdot \text{H}_2\text{O}$, the *potassium* salt,
 $\text{K}_2\text{O} \cdot 3\text{VO}_2 \cdot 2\text{SO}_2$,

the *sodium* salt, $\text{Na}_2\text{O}, 3\text{VO}_2, 2\text{SO}_2, 4\text{H}_2\text{O}$, and the *zinc* salt, $\text{ZnO}, 3\text{VO}_2, 2\text{SO}_2$, were prepared.

If a metavanadate is reduced in solution with sulphur dioxide and then an alkali sulphite added, a series of *green* alkali vanadyl sulphites, $\text{R}_2\text{O}, \text{VO}_2, 2\text{SO}_2, x\text{H}_2\text{O}$, is obtained on evaporation. The *ammonium* salt, $(\text{NH}_4)_2\text{O}, \text{VO}_2, 2\text{SO}_2, 2\text{H}_2\text{O}$, the *potassium* salt,



and the *sodium* salt, $\text{Na}_2\text{O}, \text{VO}_2, 2\text{SO}_2, 5\text{H}_2\text{O}$, have been prepared.

One mol. of ammonium vanadate was boiled with the equivalent quantity of barium hydroxide until the ammonia was completely expelled. The suspension of barium vanadate was reduced with sulphur dioxide:— $\text{Ba}(\text{VO}_3)_2 + \text{SO}_2 = \text{BaSO}_4 + 2\text{VO}_2$. After filtration, the liquid, on evaporation in a current of sulphur dioxide, gave a microcrystalline, dark blue powder of *vanadyl sulphite*, $3\text{VO}_2, 2\text{SO}_2, 4\cdot5\text{H}_2\text{O}$. This salt probably belongs to the "blue" series referred to above, and in analogy with the former formula its composition may be represented by $\text{H}_2\text{O}, 3\text{VO}_2, 2\text{SO}_2, 3\cdot5\text{H}_2\text{O}$. J. McC.

Regularities in the Composition of Halogen Double Salts.

II. FRITZ EPHRAIM (*Ber.*, 1903, 36, 1815—1824. Compare this vol., ii, 418).—To test the regularities adduced by the author in his first communication, the double haloids of quinquivalent arsenic and antimony are suitable (compare Weinland and Feige, this vol., ii, 218). Various double salts of antimony trichloride and tribromide with haloids of the alkali metals, which have been previously described by Benedict, Wheeler, Remsen, and others, are regarded by the author as having incorrect compositions assigned to them. The following list of double salts of tervalent antimony is quoted :

$\text{SbF}_3, 1\cdot5\text{LiF}$	$\text{SbF}_3, 2\text{NH}_4\text{F}$	$\text{SbF}_3, 3\text{NaF}$	$\text{SbF}_3, 2\text{KF}$
—	$\text{SbCl}_3, 2\text{NH}_4\text{Cl}$	$\text{SbCl}_3, \text{NaCl}$	$\text{SbCl}_3, 2\text{KCl}$
—	—	—	$\text{SbBr}_3, 2\text{KBr}$
—	$\text{SbI}_3, 4\text{NH}_4\text{I}$	$2\text{SbI}_3, 3\text{NaI}$	$2\text{SbI}_3, 3\text{KI}$
—	—	—	$\text{SbF}_3, 2\text{CsF}$
$\text{SbCl}_3, 2\text{RbCl}$	$\text{SbCl}_3, \text{BaCl}_2$	—	$2\text{SbCl}_3, 3\text{CsCl}$
$\text{SbBr}_3, 2\text{RbBr}$	—	—	—
$2\text{SbI}_3, 3\text{RbI}$	—	—	$2\text{SbI}_3, 3\text{CsI}$

$\text{SbCl}_3, 2\text{LiCl}, 5\text{H}_2\text{O}$ crystallises in deliquescent needles.

The following are the new compounds described : $\text{SbCl}_3, 2\text{LiCl}, 6\text{H}_2\text{O}$; $\text{SbCl}_3, \text{LiCl}_2, 6\text{H}_2\text{O}$; $\text{SbCl}_3, \text{BeCl}_2, 3\text{H}_2\text{O}$; $\text{SbCl}_3, \text{BeCl}_2, 4\text{H}_2\text{O}$; $\text{SbCl}_3, \text{MgCl}_2, 5\text{H}_2\text{O}$; and $2\text{SbCl}_2, \text{MgCl}_2$. A. McK.

Mineralogical Chemistry.

Artificial Production of Minerals by Sublimation. HERMANN TRAUBE (*Zeit. Kryst. Min.*, 1903, 37, 664; from *Centr. Min.*, 1901, 679—683).—Substances with high boiling points may be sublimed at temperatures below their boiling points by heating them in company with substances having lower boiling points. Thus, by heating cerium, didymium, lanthanum, calcium, and lead molybdates or tungstates or barium sulphate at 1400° with a mixture of sodium and potassium chlorides, these substances were sublimed either as pure crystals or as mixed crystals. L. J. S.

Mineral Analyses. FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1903, 37, 500; from *Zeit. chem. Ind. Prag.*, 1901, 155—159).—Dolomite as a thin, fibrous encrustation on serpentine from Hrubsic, Moravia; the fibres are elongated parallel to the rhombohedron edge:

CaCO ₃ .	MgCO ₃ .	MnCO ₃ .	FeCO ₃ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	H ₂ O.	Insol.	Total.
54·21	37·84	3·05	2·56	0·22	0·08	0·12	1·87	99·95

Wollastonite as fibrous aggregates in limestone from Bystré, Bohemia:

SiO ₂ .	CaO.	MgO.	MnO.	Al ₂ O ₃ .	H ₂ O.	Total.
51·45	46·82	0·47	trace	0·81	0·56	100·11

Manganite as an earthy filling of crevices in limestone at Ingrowitz, Moravia: MnO(OH), 84·79; MnO, 8·45; insol., 6·65 = 99·89; formula, 5MnO(OH), MnO₂. L. J. S.

Monazite, Xenotime, Senaite, and Native Zirconia from Brazil. EUGEN HUSSAK and J. REITINGER (*Zeit. Kryst. Min.*, 1903, 37, 550—579).—*Monazite*.—Opaque, nut-brown crystals from the diamantiferous sands of Bandeira do Mello, Rio Paraguassú, Bahia, gave, on analysis, the results under I; sp. gr. 5·012. Transparent, citron-yellow to honey-yellow crystals from the auriferous sands of Bandeirinha, Diamantina, Minas Geraes, gave II; sp. gr. 4·960. The absence of silica in the unaltered crystals from the latter locality indicates that the thorium is not present as silicate (thorite), as has been suggested; the general formula for the mineral is therefore $\alpha(\text{Ce, La, Nd, Pr})\text{PO}_4, \gamma\text{Th}_3(\text{PO}_4)_4$:

	P ₂ O ₅ .	Ce ₂ O ₃ .	Nd ₂ O ₃ .	(La, Pr) ₂ O ₃ .	ThO ₂ .	ZrO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	SiO ₂ .	H ₂ O.	Total.
I.	25·51	32·14	15·38	10·61	10·05	0·60	1·79	0·84	0·20	2·63	0·92	100·59
II.	29·18	32·46	16·81	19·21	1·09	—	0·61	—	0·10	—	—	99·46

Xenotime.—The unaltered crystals of prismatic habit from Dattas, near Diamantina, have recently been shown to have the composition 3P₂O₅, SO₃, 3R₂O₃ (Abstr., 1901, ii, 395), and on this account the name "hussakite" was proposed. It is now pointed out that this name

cannot replace the older name xenotime. Cloudy, yellow crystals of pyramidal habit found in the sands derived from the weathering of gneiss in the neighbourhood of the town of São Paulo gave analysis III :

	SiO ₂ .	SO ₃ .	P ₂ O ₅ .	Yttrium earths.	Fe ₂ O ₃ .	Total.
III.	0·41	1·19	32·72	61·79	3·55	99·66

Native Zirconia.—The following analyses are given of the so-called "favas" from the augite-syenite, district of Serra de Caldas, Minas Geraes (Abstr., 1899, ii, 432); IV, a light brown pebble of sp. gr. 4·850; V, a slate-grey pebble of sp. gr. 5·245. These are no doubt alteration products of zircon, which occurs abundantly in the augite-syenite. At the same place, there also occurs on the weathered syenite a crust with a radially fibrous structure and smooth, shining surface; this has sp. gr. 5·538, and the composition given under VI; it appears to be a new modification of zirconia distinct from baddeleyite.

	ZrO ₂ .	SiO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	MnO.	CaO.	H ₂ O.	Total.
IV.	81·75	15·49	0·50	1·06	0·85	—	—	0·63	100·28
V.	93·18	1·94	0·61	2·76	0·64	—	—	0·47	99·60
VI.	97·19	0·48	0·48	0·92	0·40	trace	trace	0·38	99·85

Senaite.—Since the publication of the original description (Abstr., 1898, ii, 439), this mineral has been shown to be widely distributed in the diamantiferous sands of the neighbourhood of Diamantina; the following new analyses (VII and VIII) of unaltered crystals are given. These results agree with the formula (Fe,Mn,Pb,Mg)O,TiO₂, and, in connection with the crystalline form, prove that senaite is isomorphous with pyrophanite, geikielite, and ilmenite:

	TiO ₂ .	FeO.	MnO.	PbO.	MgO.	ZrO ₂ .
VII.	52·11	26·97	10·42	10·86	0·32	trace
VIII.	50·32	21·99	17·58	9·62	—	0·84

Full details are given of the methods employed in the analysis of each of the minerals described. L. J. S.

Analysis of Anapaite. JOSEF LOCZKA (*Zeit. Kryst. Min.*, 1903, 37, 438—441).—The following new analysis is given of this recently described mineral (Abstr., 1902, ii, 268; this vol., ii, 303):

CaO.	FeO.	Fe ₂ O ₃ .	P ₂ O ₅ .	CO ₂ .	H ₂ O.	Total.	Sp. gr.
28·32	17·49	0·84	34·36	0·62	18·64	100·27	2·85

L. J. S.

Degree of Hydration of Cupro-uranite. YNGVE BUCHHOLZ (*Centr. Min.*, 1903, 362—365).—Cupro-uranite from Redruth, Cornwall, was found to contain 21·51 per cent. of water, corresponding with 12H₂O, instead of 8H₂O as usually given. The mineral loses 4H₂O in the desiccator, 1H₂O at 95°, 4H₂O at 148—156°, 2H₂O at about 220°, and the last molecule at a red heat. Calco-uranite also probably contains 12H₂O. L. J. S.

Studies on the Formation of Oceanic Salt Deposits. XXXI. The Lower Temperature Limit of Formation of Vanthoffite at 46°. JACOBUS H. VAN'T HOFF and G. JUST (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 499—503).—Löweite, $\text{Mg}_2\text{Na}_4(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$, was prepared by evaporating at 55—60° a saturated solution of sodium chloride, blödite (astracanite), magnesium sulphate, and leonite, to which was added a solution containing equivalent quantities of magnesium sulphate and sodium sulphate. Blödite first separates, but after 7 days a salt is deposited which contains 14·8 per cent. of water and is löweite.

The transition temperature of blödite into löweite in presence of sodium chloride is 58—59°, as was proved by a tensimetric examination. By a dilatometric study of a mixture of blödite and mirabilite, it was proved that in presence of sodium chloride these form vanthoffite at 49°. The lowest temperature of formation of vanthoffite was found to be 46°.

The upper temperature limit of existence of blödite was proved, both tensimetrically and dilatometrically, to be 59°. J. McC.

Formation of Oceanic Salt Deposits. XXXII. J. H. VAN'T HOFF and W. MEYERHOFFER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 678—684).—Below are tabulated the higher limits of temperature at which the following salts may be formed in the presence or absence of sodium chloride; the last column gives the product which is formed above these temperatures:

	With NaCl.	Without NaCl.	
Mirabilite, $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$	18°	32½°	Thenardite, NaSO_4 .
Picromerite, $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	26	47½	Leonite, $\text{MgK}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
Epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	31	48	(Hexahydrate), $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.
(Hexahydrate), $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	35½	67½	Kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$.
Blödite, $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$...	59	71	Löweite, $\text{MgNa}_2(\text{SO}_4)_2 \cdot 2½\text{H}_2\text{O}$.
Leonite, $\text{MgK}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$...	61½	89	Langbeinite, $\text{Mg}_2\text{K}_2(\text{SO}_4)_3$.
Kainite, $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$...	83	85	"Hartsalz," $\text{MgSO}_4 + \text{KCl}$.

L. J. S.

Composition and Synthesis of Römerite: Ferropallidite. RUDOLF SCHARIZER (*Zeit. Kryst. Min.*, 1903, 37, 529—549).—Römerite was prepared by allowing a mixture of powdered ferrous sulphate and acid ferric sulphate to remain in contact with moist air for several months. The reddish-brown, crystalline powder so obtained has the composition $\text{Fe}''\text{Fe}'''(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$. Between 70° and 130°, the material loses $12\text{H}_2\text{O}$ and assumes a bluish-black colour; the remaining water is expelled only at a much higher temperature.

Two analyses of native romerite from Chili agree with the new formula given above. In material from Rammelsberg, Harz, a portion of the ferrous iron is replaced by zinc and magnesium, as shown by the following analysis (I):

	SO ₃ .	Fe ₂ O ₃ .	FeO.	ZnO.	CoO.	MgO.	H ₂ O.	Insol.	Total.
I.	39·71	19·77	5·80	3·06	trace	0·25	31·17	0·04	99·80
II.	39·41	19·59	3·29	6·60	—	—	31·38	—	100·27

An artificial zinc-römerite was prepared by substituting zinc sulphate for ferrous sulphate in the method given above; the product is yellow in colour and has the composition given under II.

Ferropallidite.—This name was given to a white, granular mineral which occurs with römerite at Alcapa rossa, Calama, Chili. It is birefringent, and has the composition FeSO₄·H₂O, as given by analysis III. By treating commercial ferrous sulphate with concentrated sulphuric acid, a ferrous sulphate containing 13·08 per cent. of water was obtained:

	SO ₃ .	Fe ₂ O ₃ .	FeO.	H ₂ O.	Insol.	Total.
III.	46·66	0·92	40·94	10·33	0·87	99·72

L. J. S.

Nephrite from New Zealand. ARTHUR DIESELDORFF (*Zeit. Kryst. Min.*, 1903, 37, 656; from *Centr. Min.*, 1901, 334—344).—Small nodular masses of nephrite (analysis I) were found in the serpentine of d'Urville Island, Cook Strait; microscopical examination shows this to be secondary uraltic nephrite. Pebbles of nephrite (analysis II) are also found on the shore of the island:

	SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.	Cu.	Cr, Mn.	Total.
I.	55·59	1·43	6·15	12·93	21·24	2·35	0·17	traces	99·86
II.	52·77	1·88	4·36	15·39	21·17	2·77	—	—	98·34

Nephrite (jade) is considered to be a mixture of actinolite and augite.

L. J. S.

[Amphibole-anthophyllite from Sweden.] RICHARD BECK (*Zeit. Kryst. Min.*, 1903, 37, 515; from *Tsch. Min. Mitth.*, 1901, 20, 382—389).—This is light greyish-brown in colour and occurs in the Långfalls zinc mine near Räfåla. It is monoclinic with the typical hornblende cleavage; the angle of optical extinction does not exceed 6°; optically positive. Sp. gr. 3·24. Analysis by K. Kolasnikoff gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	K ₂ O.	H ₂ O.	PbS.	Total.
52·89	1·59	7·10	12·60	22·17	2·23	0·71	0·17	99·46.

L. J. S.

Analyses of Moravian Minerals. FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1903, 37, 500; from *Chem. Blätter, Prag*, 1901, 233—238).—Bronzite (I) from Mohelno is pale green, and when fresh has a vitreous lustre; only when altered does it show a semi-metallic, pearly lustre. It occurs as nests and veins in serpentine.

Diallage (II), from Naměst, forms a coarse-grained, dark brown rock, probably in association with serpentine :

	SiO ₂ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	Total.
I.	54.39	1.70	7.36	trace	1.64	34.52	0.10	99.71
II.	48.63	1.84	13.35	2.29	20.15	13.31	—	99.57

L. J. S.

Composition of Minerals of the Bole Group. FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1903, 37, 499 ; from *Zeit. chem. Ind. Prag.*, 1901, 225—230).—The following analyses are given of clays of different colours (I, siskin-green ; II, IV, yellow-brown ; III, red-brown) and characters, from limestone beds in Moravia and Bohemia :

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	Alkalis.	H ₂ O.	Organic matter.	Total.
I.	45.40	27.05	1.75	—	0.96	trace	—	24.60	—	99.76
II.	41.28	23.75	9.60	trace	1.02	0.26	—	24.32	—	100.23
III.	39.50	22.02	12.86	0.07	0.90	0.12	trace	24.97	—	100.44
IV.	44.59	26.38	12.29	0.11	1.20	trace	trace	15.88	trace	100.45
V.	42.31	23.56	9.83	0.09	3.25	1.50	0.28	16.16	2.82	99.80

Each of these clays, when digested with dilute hydrochloric acid, leaves a white, scaly residue. Deducting Fe(OH)₃ from the above results, analyses I—III give the formula H₂Al₂Si₃O₁₀.4H₂O, and IV and V give H₂Al₂Si₃O₁₀.2H₂O.

L. J. S.

Anorthite Bomb from St. Christopher, West Indies. G. FELS (*Zeit. Kryst. Min.*, 1903, 37, 450—460).—A volcanic bomb from the island of St. Christopher, consisting mainly of anorthite (analysis I), with hypersthene (II), black hornblende (III), some magnetite, and a little olivine, contains in drusy cavities well-developed crystals of colourless, glassy anorthite and of hypersthene, of which crystallographic descriptions are given. The hypersthene crystals are black, but reddish-brown in transmitted light ; the cleavage is imperfect and the fracture conchoidal :

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.	Sp. gr.
I.	44.17	—	35.06	—	0.58	18.84	0.57	0.43	1.21	0.59	101.45	2.73
II.	50.54	—	3.94	0.90	17.08	1.82	25.71	0.55	0.79	—	101.33	3.45
III.	43.26	0.29	13.15	2.27	10.50	12.11	15.06	0.57	3.49	0.21	100.91	3.17

L. J. S.

Red Zoisite from Moravia. F. SLAVÍK (*Zeit. Kryst. Min.*, 1903, 37, 664 ; from *Centr. Min.*, 1901, 687—690).—A description is given of the red zoisite which occurs as bands in association with crystalline limestone in contact with granite-gneiss at Třebíč ; analysis by F. Kovář gave :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	H ₂ O.	Total.
38.91	29.38	4.46	0.17	25.18	0.44	2.06	100.60

The occurrence of zoisite at other localities in Moravia is noted.

L. J. S.

The Mineral Deposits in the Biotite-protogine of the Aar Massive, Switzerland. JOH. KOENIGSBERGER (*Zeit. Kryst. Min.*, 1903, 37, 643—650; from *Jahrb. Min.*, 1901, *Beil.-Bd.*, 14, 43—119).—A detailed account is given of this mass of "protogine," and of the several secondary minerals which occur in the crevices of the rock. Near these crevices, the biotite (sp. gr. 3.19; analyses I and II) is altered to chlorite, and the plagioclase to epidote, kaolin, and sillimanite. Analyses III—VI are of chlorite from the crevices:

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Mn ₂ O ₃	K ₂ O	Na ₂ O	Li ₂ O	H ₂ O	P ₂ O ₅	Total
I.	36.5	0.2	21.1	13.0	12.5	0.8	6.1	1.5	3.4	0.3	—	2.9	0.5	98.8
II.	36.65	0.50	16.65	12.10	12.60	0.80	6.15	1.50	8.30	—	—	2.90	0.70	98.85
III.	25.50	trace	22.25	22.85	12.20	0.20	6.30	trace	traces	—	—	10.60	—	99.90
IV.	25.40	—	—	22.35	12.00	—	6.10	—	—	—	—	10.50	—	—
V.	29.30	—	16.25	28.40	1.80	—	7.75	1.85	—	1.10	—	12.70	—	99.15
VI.	27.70	—	14.60	31.50	(1.80)	—	7.10	1.70	—	2.05	0.30	12.85	—	99.60

The rock is considered to have been altered by the action of hot waters containing air and carbon dioxide in solution, and the secondary minerals to have crystallised out in the crevices from the solutions so formed. The succession and paragenesis of the secondary minerals is dealt with.

L. J. S.

Meteoric Iron from Augusta Co., Virginia. H. D. CAMPBELL and JAMES L. HOWE (*Amer. J. Sci.*, 1903, [iv], 15, 469—471).—The history of this mass of iron, which weighs rather more than 7 kilograms, is unknown. The gas extracted by heating in a vacuum was found by W. Ramsay to consist mainly of methane, with a little hydrogen and argon, and possibly helium. Analysis by J. E. Whitfield gave:

Fe.	Ni.	Co.	Cu.	P.	S.	C.	Si.
91.376	7.689	0.610	0.066	0.161	0.006	0.047	0.045

In structure and composition, this iron differs somewhat from the Staunton irons, also from that from Augusta Co., Virginia, but as it may possibly belong to the same fall, it is called "Staunton, No. 7."

L. J. S.

Physiological Chemistry.

Artificial Parthenogenesis. E. P. LYON (*Amer. J. Physiol.*, 1903, 9, 308—318).—Experiments carried out at Naples, where observers have not been, as a rule, able to repeat Loeb's results. Some experiments failed, but on the whole Loeb's conclusions are confirmed.

W. D. H.

[Action of Gastric Juice on Fats.] ELOPHE BÉNECH and L. GUYOT (*Compt. rend. Soc. Biol.*, 1903, 55, 719—721, 721—722).—Gastric juice collected an hour after a test-meal contains a lipase,

which is shown to possess the power of hydrolysing monobutyrin. The presence of the normal amount of hydrochloric acid favours its action, and it obeys Schutz's law. W. D. H.

The Action of Pure Gastric Juice (from the Dog) on Hæmoglobin and Globin. SERGEI SALASKIN and KATHARINA KOWALEVSKY (*Zeit. physiol. Chem.*, 1903, 38, 567—584).—Attention is again drawn to the fact that the prolonged action of gastric juice is able to produce crystalline hydrolytic products from proteids. In the present research, the proteids employed were crystallised hæmoglobin from the horse, and globin prepared from it. Gastric juice obtained by a fistula was employed. Among the products ultimately separated were alanine, leucine, phenylalanine, glutamic acid, aspartic acid, tyrosine, and pyrrolidinecarboxylic acid. W. D. H.

Peptic Proteolysis. WILLIAM J. GIES (*Proc. Amer. physiol. Soc.*, 1903, xvii; *Amer. J. Physiol.*, 9).—Numerous digestion experiments with various equi-dissociated acids of the same conductivity as a 0.2 per cent. solution of hydrochloric acid give more variable results. The nature of the acid itself is important. The anions modify the action of the common cation, the SO_4 anion being especially antagonistic in its influence. W. D. H.

Trypsin. KARL MAYS (*Zeit. physiol. Chem.*, 1903, 38, 428—512).—Various methods of extraction of the pancreas are described, and more active preparations are obtained when the extraction is carried out at room temperature than at body temperature. Improvement and deterioration of the extracts were observed as in Vernon's experiments. By using strong salt solution as the extracting agent, and precipitating the enzyme by saturation with different neutral salts, precipitates with tryptic power were obtained. On being dissolved, these are precipitable by dialysing against distilled water. The most remarkable fact in connection with these preparations is that they are practically proteid-free. W. D. H.

Liberation of Trypsin from Trypsin-zymogen. E. HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 34—42).—Heidenhain's opinion that acids liberate trypsin from trypsinogen is incorrect; they prevent the liberation. The mistake arose from using glycerol extracts, and acid decreases the injurious effect of that reagent. No free trypsin is present in the pancreatic secretion; the liberation of that enzyme is the work of the intestinal juice; gastric juice is not able to effect it. W. D. H.

Differences of Potential between Blood and Serum, and between Normal and Laked Blood. GEORGE N. STEWART (*Amer. J. Physiol.*, 1903, 9, 262—264).—After such hæmolytic agents as sapotoxin have produced marked liberation of electrolytes from the corpuscles, the differences of potential between blood so treated and unlaked blood are very small. No definite differences could be detected

between defibrinated blood, or a blood sediment rich in corpuscles, and the serum separated from it. W. D. H.

Disappearance of Carbon Monoxide from the Blood of Persons Poisoned by that Gas. LÉON GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 761—763).—Several cases of undoubted carbon monoxide poisoning are described, most of which ended fatally. The remarkable fact noted in some of these is that the usual tests for carbon monoxide hæmoglobin failed. No adequate explanation of this is forthcoming. W. D. H.

Glycerol in the Blood. MAURICE NICLOUX (*Compt. rend.*, 1903, 136, 1576—1577).—The small amount of glycerol previously shown to exist in normal blood is not influenced in the dog by the state of digestion, and is approximately the same whether the animals are fasting or in a state of full digestion of a fatty meal. W. D. H.

Saponifying Action of Serum on Esters. MAURICE DOYON and ALBERT MOREL (*Compt. rend. Soc. Biol.*, 1903, 55, 682—683).—Whilst blood serum saponifies monobutyrim, it does not saponify normal fats such as olein. The saponifying action of horses' serum on ethyl acetate, propionate, butyrate, valerate, hexoate, succinate, benzoate and salicylate, amyl salicylate, phenetole, mono-, di-, and tri-butyrim, and triacetin was studied. Comparative estimations of the amount of hydrolysis were made with each in presence of sodium carbonate on the one hand and of sodium carbonate and serum on the other. Phenetole and ethyl salicylate were not hydrolysed at all; amyl salicylate was feebly hydrolysed. A. McK.

Oxidation and Resolution in the Animal Organism. ALEXIS BACH and F. BATTELLI (*Compt. rend. Soc. Biol.*, 1903, 55, 732—733).—The chemical transformations in the body are to be mainly attributed to two sets of enzymes, hydrolytic and oxidising. In the present paper, dextrose is mainly alluded to. The liberation of carbon dioxide is stated to be always due to hydrolysis, never to oxidation; the liberation of water is always oxidative, and is thus an important factor as a source of energy. W. D. H.

Some Conditions of the Oxidation of Salicylaldehyde by [Animal] Organs and Extracts of Organs. J. E. ABELOUS and JULES ALOY (*Compt. rend.*, 1903, 136, 1573—1576. Compare *Arch. Physiol.*, 1894—1898).—The results of experiments which were made almost exclusively with horse and calf liver showed that the oxidation of salicylaldehyde takes place in the extracts more readily in a vacuum than in presence of air. The presence both of free oxygen and of reducing agents diminishes the oxidation or stops it altogether. The necessary oxygen is furnished by the compounds which the oxidising ferment dissociates. This dissociation seems to be retarded by certain substances, such as alkali nitrates and nitrites.

N. H. J. M.

An Enzyme in the Hen's Egg which reduces Nitrates. J. E. ABELOUS and JULES ALOY (*Compt. rend. Soc. Biol.*, 1903, 55, 711—712).—The egg contains a soluble ferment able to reduce nitrates, as do other animal tissues. The amount is slight at first, but increases at the fourth or fifth day, and markedly so after that.

W. D. H.

Applications of Physical Chemistry to the Study of Toxins and Antitoxins. SVANTE ARRHENIUS and THORVALD MADSEN (*Zeit. physikal. Chem.*, 1903, 44, 7—62).—The hæmolytic action of various amounts of hæmolysin is proportional to the square of concentration of the toxin. This action was compared with that of bases, neutral salts and proteids, and the results given in tables and curves show that the formation of dissociable compounds between the corpuscular contents and the reagents will account for many of the phenomena. The influence of temperature was also investigated. Among the numerous conclusions drawn, the following are of interest: normal serum is hæmolytic because it contains a large amount of albumin; the amount of antitoxin in it is small; egg-albumin is shown to be antagonistic to tetanolysin (the lysin mainly employed); by the union of a gram-molecule of tetanolysin with the same amount of its antitoxin, more than 6000 calories are developed; the result of such a union is the formation of two molecules of the compound.

W. D. H.

Soluble Ferments in the Human Kidney. BATTESTI and BARRAJA (*Compt. rend. Soc. Biol.*, 1903, 55, 820—821, 821—822).—Human kidneys, obtained as fresh as possible from accident cases, were extracted with glycerol and 1 per cent. of sodium fluoride added. In the extract, the certain presence of amylase, sucrase, casease, and oxydase, and the doubtful presence of a peptic ferment and lipase were noted. Urease and reducing ferment were absent.

The renal pulp causes the decomposition of salol, benzonaphthol, acetanilide, guaiacol, and sodium salicylate; this confirms Gérard's observations on the kidney tissue of the horse. It is also shown that decompositions of aspirine, tannigen (diacetyl gallic acid), tannin, and mercury albuminate are also effected.

W. D. H.

Presence of Hydrogen Sulphide in Boiled Milk. FRANZ UTZ (*Milch-Zeit.*, 1903, 32, 354—355).—The author states that hydrogen sulphide is formed when milk is boiled. It may be detected either by means of lead acetate paper or by Ganassini's reagent (compare this vol., ii, 40).

W. P. S.

Secretin and Lymph-flow. LAFAYETTE B. MENDEL and HENRY C. TREACHER (*Proc. Amer. Physiol. Soc.*, 1903, xv—xvi; *Amer. J. Physiol.*, 9).—Secretin produces an increased flow of lymph from the thoracic duct, which is independent of alterations in general blood-pressure.

W. D. H.

Experiments on Urine. G. H. A. CLOWES (*Amer. J. Physiol.*, 1903, 9, 319—343).—The subject treated is the relationship between the freezing point depression and the specific gravity of urine under varying conditions of metabolism, and its chemical value in the estimation of sugar and albumin. In normal urine, the depression of the freezing point is directly proportional to the sp. gr., and may be ascertained from the latter by multiplying the figures after the decimal point by 75. In pathological urine containing no sugar or albumin, the same is approximately true also. When the excretion of chlorides is small, as in cancer and typhoid, the effect exerted on the freezing point depression is not so great as would be expected from the removal of so many small ions. In diabetic urines, the sugar may be readily estimated by determining the lowering of the freezing point and calculating it from the sp. gr.; the difference between the two multiplied by 6 gives the percentage of sugar. The percentage of albumin may be estimated by determining the sp. gr. and freezing point in the urine before and after removal of the proteid by acidifying and boiling. The decimal portion of the sp. gr. after boiling is multiplied by the freezing point before boiling and divided by that after boiling. The result is subtracted from the original sp. gr. and the difference multiplied by 400.

W. D. H.

Acidity of Urine. OTTO FOLIN (*Amer. J. Physiol.*, 1903, 9, 265—278).—A discussion on this much debated subject, illustrated with records of experiments.

W. D. H.

Diuretic Action of Hypertonic Salt Solutions. TORALD SOLLMANN (*Proc. Amer. Physiol. Soc.*, 1903, xiii—xiv; *Amer. J. Physiol.*, 9).—The diuretic effect of molecular salt solutions is usually proportional to their osmotic pressure. Hypertonic solutions in the excised kidney increase, whilst hypotonic solutions decrease or arrest, urine formation. The diuretic effect of saline injections is partly explained by increased fluidity and quickened circulation of the blood through the kidney. The superior effect of hypertonic solutions is partly physical, and is explained by the dehydration and shrinkage of the kidney tissue and the more rapid circulation so produced.

W. D. H.

Effect of Saline Injections on Urinary Chlorides. TORALD SOLLMANN (*Proc. Amer. Physiol. Soc.*, 1903, xii—xiii; *Amer. J. Physiol.*, 9).—The essential cause of diminished chlorides in the urine is a lowered percentage of chlorine in the fluid portion of the blood. The two quantities are not proportional, and it is suggested that part of the chlorides in the blood are in combination with proteid in the blood. If excised kidneys are perfused with a sodium chloride solution, the urine formed contains the same amount of salt; but if the perfused fluid is salt solution and blood, the amount in the urine is never so high.

W. D. H.

Effect of Alcohol on Uric Acid Excretion. RUSSELL H. CHITTENDEN and S. P. BEEBE (*Proc. Amer. Physiol. Soc.*, 1903, xi—xii; *Amer. J. Physiol.*, 9).—Pure alcohol diluted with water given to men

during fasting produces diuresis and a decreased excretion of uric acid; given with meals, there is an increase in the excretion of this substance; this indicates that the effect is due to a disturbance in the metabolism of the purin bases of the food. The same amount of alcohol given in the form of beer or wine produces more effect, showing that it is in part due to substances other than alcohol. W. D. H.

Influence of Quinic Acid on Uric Acid Excretion. W. A. TALTAVALL and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1903, xvi; *Amer. J. Physiol.*, 9).—Quinic acid does not materially affect the uric acid output in dogs. This result agrees with that of Huffer, and is at variance with those of earlier observers. W. D. H.

Behaviour of Allantoin in the Body. A. M. LUZZATO (*Zeit. physiol. Chem.*, 1903, 38, 537—544).—In dogs fed on meat, allantoin is a constant constituent of the urine. If they are fed on uric acid, it also appears. If they are fed on thymus, it appears as a sediment. If allantoin itself is given, 70 per cent. is excreted unchanged (Min-kowski); but this proportion is much smaller in men. In the present research, parallel researches were carried out on a dog and a rabbit, allantoin being added to the food; in the dog, the major part was recovered in the urine, in the rabbit none. In the rabbit, it appears to be badly absorbed, and to be in part excreted as oxalic acid.

W. D. H.

Origin of Indican in the Animal Body. HARRY SCHOLZ (*Zeit. physiol. Chem.*, 1903, 38, 513—536).—An increase of indican in the urine cannot be produced by an artificially increased proteid katabolism. The same is true for the excretion of phenol. No other cause for the appearance of indican in the urine was discovered other than putrefaction brought about by bacteria.

W. D. H.

Indoxyl in Pathological Urines. JULIUS GNEZDA (*Compt. rend.*, 1903, 136, 1406—1408. Compare Abstr., 1902, ii, 339).—Attention is drawn to the fact that urines in cases of pneumonia and other febrile disorders, which are usually rich in urobilin, contain indoxyl also. The presence of urobilin prevents the usual indican reactions.

W. D. H.

Indoxyl in Urine. LOUIS MAILLARD (*Compt. rend.*, 1903, 136, 1472—1473).—A criticism of Gnezda's methods and results (see preceding abstract).

W. D. H.

Chloroformic Urinary Pigments. LOUIS MAILLARD (*Compt. rend. Soc. Biol.*, 1903, 55, 695—697, 777—779. Compare Abstr., 1901, ii, 407; 1902, i, 371).—On acidifying normal urine with hydrochloric acid and extracting with chloroform, a blue pigment, *hemi-indigotin*, $C_{16}H_{10}O_2N_2$, goes into solution. This is derived from indoxyl, is unstable, and in an acid medium is transformed into indirubin, and in an alkaline into indigotin. In some circum-

stances, a brown pigment is obtained, but this also is an indoxyl derivative. Pigments derived from scatoxyl are not believed in.

W. D. H.

Cystin Diathesis in Families. EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1903, 38, 557—561).—Attention is drawn by the description of cases to the already well-known fact that the metabolic anomaly which results in cystin urea is hereditary.

W. D. H.

[**Puerperal Eclampsia.**] ALBERT CHARRIN and ROCHÉ (*Compt. rend.*, 1903, 136, 1593—1596).—The disorders of the puerperal state such as eclampsia are attributed to poisons formed within the body; whether these are of mineral or organic (alkaloidal) nature and whether anti-substances are produced is left uncertain.

W. D. H.

Physiological Action of Optical Isomerides. ARTHUR R. CUSHNY (*Proc. Amer. Physiol. Soc.*, 1903, xiv; *Amer. J. Physiol.*, 9).—*d*-Hyoscyamine is practically devoid of action on nerve terminations in salivary glands, heart, and pupil. *l*-Hyoscyamine acts very strongly. Atropine, the racemic form, has an intermediate action. Probably in the body the two optically active forms are liberated, and the nerve terminals can differentiate between them.

W. D. H.

Effects of Subcutaneous Injection of Suprarenal Extract. S. J. MELTZER and CLARA MELTZER (*Amer. J. Physiol.*, 1903, 9, 252—261).—A distinctly toxic dose of suprarenal extract given subcutaneously causes blanching of the rabbit's ear; a medium dose causes distinct dilatation of its blood-vessels if the nerves are intact, but constriction if the vaso-motor nerves are cut. Adrenalin appears to be but little oxidised in the subcutaneous tissues.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Changes Correlative with the Formation of Alcohol in Fermenting Saccharine Juices. Distinction between Alcoholated Musts and true Vinous Liquors. ARMAND GAUTIER and GEORGES HALPHEN (*Compt. rend.*, 1903, 136, 1373—1379).—The changes which take place in nitrogen compounds, in the volatile and total acids, in the nature of the sugars, and in the variations of glycerol during the fermentation of sugars in several grape juices have been studied.

As fermentation proceeds, the ammoniacal nitrogen diminishes and finally disappears; the organic basic nitrogen remains almost constant, and the proteid nitrogen suffers hardly any change. The amount of volatile acid present increases as the fermentation proceeds. In the

original juice, only a trace of glycerol is present, but it increases proportionally with the alcohol.

These observations can be utilised to distinguish between an alcoholic liquor prepared artificially and a true fermented liquid.

J. McC.

Action of Abietic Acid on Ferments. JEAN EFFRONT (*Compt. rend.*, 1903, 136, 1556—1557).—Lactic or butyric ferments or yeast may be grown on a nutritive medium containing abietic acid without any special action becoming evident. But if such a nutritive medium be inoculated with a mixture of ferments a selective growth takes place. If the mixture contains much yeast and little lactic ferment, scarcely any development of the lactic ferment takes place, but the yeast grows rapidly. Quite the reverse takes place if the mixture contains much lactic ferment and little yeast. The same effect is produced if colophony is used in place of abietic acid, but it must be free from volatile constituents.

J. McC.

Some Constituents of Yeast. OSCAR HINSBERG and E. ROOS (*Zeit. physiol. Chem.*, 1903, 38, 1—15. Compare Nägeli and Löw, *Annalen*, 1878, 193, 337).—Bottom yeast is extracted with hot alcohol, the alcohol distilled off, and the residue from the extract shaken with ether after being rendered slightly alkaline with very dilute sodium hydroxide. The ethereal extract contains the fat together with minute amounts of a cholesterol and of ethereal oils. The yield of fat is some 2·3—2·8 per cent. of the yeast dried at 100°, but appears to be smaller in summer than in winter.

When hydrolysed with alkali, the fat yields a number of acids, among which are: (a) a saturated acid, $C_{15}H_{30}O_2$, crystallising in glistening plates and melting at 56°. It is almost insoluble in water and only sparingly soluble in methyl alcohol, acetic acid, or light petroleum. The acid somewhat resembles myristic acid, but is not identical with it. (b) An acid, $C_{12}H_{22}O_2$, a colourless and odourless oil, which on oxidation in contact with the atmosphere acquires a most penetrating odour. (c) An acid, $C_{18}H_{34}O_2$, a colourless oil distilling at 210—220° under 12 mm. pressure. The cholesterol, $C_{26}H_{44}O, H_2O$, contained in yeast crystallises from alcohol in colourless plates, melts at 159°, and is not identical with Schulze and Barbieri's caulosterin (*Abstr.*, 1882, 1202), although both have practically the same melting point. The essential oil contained in yeast is a colourless liquid with an odour of hyacinths, and is volatile with steam.

J. J. S.

Fermentive Decomposition of Fats, Oils, and Esters. II. KARL BRAUN and EMIL C. BEHRENDT (*Ber.*, 1903, 36, 1900—1911. Compare this vol., ii, 446).—A series of results are given showing that the fermentive action of abrin in the form of crushed seeds of *Abrus precatorius* is generally greater than that of the "ricin" of castor oil seeds; the fermentive production of free acid was studied in the case of lanolin, carnauba wax, and a number of aliphatic and aromatic esters, and it appears that it is greater in the case of fatty than in

that of benzenoid esters. Mercury, copper, and iron salts and alcohol retard the fermentation, but magnesium and alkali salts and tungsten compounds are without influence.

Emulsin or bitter almonds produce only a very slight acidity with castor oil, and the same is true of amygdalin and a mixture of amygdalin and emulsin. Black mustard seeds (*Sinapis nigra*) are slightly more fermentive, whilst the action of *Cheiranthus cheiri* is intermediate between emulsin and ricin. W. A. D.

Respiration of Sugar-beet Root. FRIEDRICH STROHMER (*Bied. Centr.*, 1903, 32, 465—469; from *Oesterr.-Ung. Zeit. Zuckerind. u. Landw.*, 1902, Heft 6).—The experiments were made with single ripe roots. The loss of sugar was always relatively greater than the loss of carbon dioxide, and there was no regular relation between the amount of sugar lost by respiration and the amount converted into other substances. The greatest loss of sugar is generally as carbon dioxide, except when shoots are formed, in which case the loss by respiration is much less than the loss due to conversion of the sugar into other compounds. It is probable that the sucrose is converted into reducing sugar before being resolved into carbon dioxide and water.

The freezing point of the roots is -1° to -1.1° , and roots may be kept at 0° for a long time without being injured.

Mechanically injured roots should be excluded when roots are stored, as the fungi which appear on the injured roots spread to others. N. H. J. M.

Nitrogen Assimilation of Wheat Grain. JOSEF ADORJÁN (*Landw. Versuchs-Stat.*, 1903, 58, 281—289. Compare this vol., ii, 94).—The amount of proteids in wheat grain and the absolute weight depend almost exclusively on external conditions, such as the amount of nitrogen in the soil and the conditions of climate. The specific characters of different varieties have only an indirect effect, the varying duration of vegetation being coincident with variations in the weather to which the crop is subjected. N. H. J. M.

Composition and Metabolism of Seedlings. ERNST SCHULZE and NICOLA CASTORO (*Zeit. physiol. Chem.*, 1903, 38, 199—258).—Seedlings of *Lupinus albus*, when kept in darkness, lost proteids, whilst the amount of asparagine increased rapidly (compare Merlis, *Landw. Versuchs-Stat.*, 48, 419). There was at the same time a loss of tyrosine and probably of leucine. The amount of arginine increased up to the fourth day and then diminished. The tyrosine, leucine, and arginine lost during this period may be partly, but cannot be mainly, utilised in the regeneration of proteids, since the proteids themselves diminish in quantity. It is more probable that they are broken up, but without elimination of free nitrogen.

In the case of the same seedlings kept with access of light, the loss of proteids is less owing to the co-operation of newly-found carbohydrates in the regeneration of proteids. The percentage of asparagine in seedlings 14 days old still remained high, whilst amino-acids were

found in very small amount, less even than in etiolated plants 18 days old.

The distribution of asparagine in seedlings 14 days old, as well as other results, indicate that asparagine is readily available for the reproduction of proteids. The relatively large amount of asparagine which remains in seedlings already green is accounted for by its synthetical formation from a decomposition product (? ammonia) of the decomposition of proteids.

N. H. J. M.

Nutrition of Plants deprived of their Cotyledons. GUSTAVE ANDRÉ (*Compt. rend.*, 1903, 136, 1401—1404).—Analyses were made of haricots, from which the cotyledons had been removed 12 days after sowing the seeds, and of normal plants. The seeds were sown on June 12th, and the seedlings were analysed at seven successive periods ending with July 7th. The following results (in grams) are those obtained at the last date, and refer to 100 plants—(a) normal, and (b) plants without cotyledons:

	Total weight.	Dry matter.	N.	Ash.	K ₂ O.	CaO.	H ₃ PO ₄ .
(a)	1316	147.8	5.20	21.54	4.819	3.681	1.493
(b)	826	88.8	3.38	15.43	4.447	3.231	1.447

N. H. J. M.

Comparisons between the Phenomena of the Nutrition of Plants without and with Cotyledons. GUSTAVE ANDRÉ (*Compt. rend.*, 1903, 136, 1571—1573. Compare preceding abstract).—Determinations of soluble carbohydrates, saccharifiable carbohydrates, and cellulose were made in the same plants at the different dates.

N. H. J. M.

Mechanism of the Saccharification of Mannans of *Phytalephas macrocarpa* by the Seminase of Lucerne. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1903, 136, 1404—1406).—*Phytalephas macrocarpa* contains a soluble ferment which is destroyed by heating at 100°. Boiled extracts yielded mannose when seminase (lucerne malt) was added, but the yield of mannose was much greater when the extract had not been previously boiled.

N. H. J. M.

Occurrence of Urea in Plants. MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1903, 24, 218—219).—Urea in considerable quantities up to 3.5 per cent. is found to exist in the capitulum of ripe specimens of *Lycoperdon Bovista*. As other components of urine, especially chlorine, were not present, the occurrence is assumed to be natural. A large number of these plants have without exception been found to contain urea.

E. F. A.

Natural Occurrence of Salicylic Acid in Strawberries and Raspberries. KARL WINDISCH (*Zeit. Nahr. Genussm.*, 1903, 6, 447—452).—The author's experiments confirm the statements of other

investigators that salicylic acid, or an ester of this acid, is present in small quantities in both strawberries and raspberries (compare Abstr., 1902, ii, 40). The amounts found were 1.1 mg. per litre of raspberry juice and 2.8 mg. per litre of strawberry juice. Several varieties of cherries, plums, currants, gooseberries, peaches, apricots, &c., were also examined, but salicylic acid was not detected. W. P. S.

Distribution of some Organic Substances in Geraniums. EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1903, 136, 1467—1469).—The amount of volatile acid diminishes from the leaves to the stems and the terpene compounds are confined entirely to the leaves. This accounts for the flowers having no odour. It is suggested that the essential oils, or at any rate the substances from which they are immediately derived, are formed in the chlorophyllous organs and then migrate to other parts of the plant, where they undergo more or less change. N. H. J. M.

Amount of Sugar contained in Cinnamon Bark. O. VON CZADEK (*Chem. Centr.*, 1903, i, 1229; from *Zeit. landw. Vers. Wes. Öst.*, 6, 524—527).—Although the addition of 3 per cent. of sucrose to cinnamon before grinding has been found to reduce the quantity of dust from 4.6 to 1 per cent., this result is preferably attained by a suitable arrangement of sieves. Stick cinnamon (*Cassia lignea* and *zeylonicum*) was found to contain not more than 2 per cent. of sugar calculated as invert sugar, and from 0.09—0.53 of sucrose. A sample of *Cassia vera* contained 6.22 per cent.; 4.19 was found in the inner portions of the bark, whilst the outer portions contained only 1.4 per cent. A sample of the bark of *Cassia vera Timor*, which resembled the Ceylon cinnamon in appearance, but had neither the taste nor the odour of cinnamon, contained 3.06 per cent. of sugar. The addition of a small percentage of sugar to cinnamon is readily detected; in many cases, it may be found in the sediment after extracting with chloroform. E. W. W.

Reserve Carbohydrates of Nutmeg and Mace. A. BRACHIN (*J. Pharm. Chim.*, 1903, [vi], 18, 16—21).—Nutmeg contains 0.56 per cent. of sucrose, and, in addition to starch, appears also to contain xylose, but no glucosides. Mace does not contain sucrose or glucosides, and on extraction with water yields a pectin having the specific rotation +240°. G. D. L.

Changes in the so-called Lead-blackening Sulphur in Relation to the Total Sulphur in Seedlings of *Lupinus angustifolius*. H. SERTZ (*Zeit. physiol. Chem.*, 1903, 38, 323—335).—The total sulphur was determined by Liebig's method, and the "lead-blackening" sulphur (that portion of proteid sulphur which is separated by boiling with alkali) by Schulz's method (*ibid.*, 1898, 25, 16). The substance was boiled for 10 hours, acidified with acetic acid, filtered, and washed.

The residue (with filter) was then fused with sodium carbonate and sodium nitrate in an iron dish.

Determinations were made in seeds and in seedlings 4, 7, 9, 11, 15, and 18 days old. The results show a considerable loss of "lead-blackening" sulphur, chiefly in the first four days. N. H. J. M.

Sarracenia Purpurea. WILLIAM J. GIES (*Chem. Centr.*, 1903, i, 1233; from *J. New York Bot. Garden*, 4, 37—39).—Attempts to isolate an enzyme or zymogen from *Sarracenia purpurea* and other insect-eating plants have not given very definite results, for whilst the glycerol extracts of one series of plants had a distinct action on fibrin in presence of hydrochloric or oxalic acid, the extracts of another series were completely inactive. The concentrated neutral glycerol extracts have a red colour, whilst the dilute extracts are practically colourless, but become green on addition of alkalis and rose-coloured with acids. The colouring matter is named *alkaverdin*. Filter-paper which has been moistened with the strong extract is colourless in the wet or dry state, and serves as an indicator for acids or alkalis. A considerable quantity of a substance which has reducing properties and can be fermented may be extracted from *Sarracenia* by means of water or solutions of salt. E. W. W.

Molasses Food and Horse Feeding. L. GRANDEAU (*Bied. Centr.*, 1903, 32, 483—486; from *J. d'Agric. prat.*, 1902, 697; 1903, 37, 177, and 208).—The results of experiments in which horses were fed with molasses bread (made with inferior cereal meal and 50—60 per cent. of its weight of green molasses) and with straw molasses showed that the two foods were of about equal value and not much less nutritious than oats. N. H. J. M.

Effect of some Mineral Substances on Cows. CLEMENS SCHULTE-BÄUMINGHAUS (*Bied. Centr.*, 1903, 32, 477—483; from *Mitt. Landw. Inst. Univ. Breslau*, 2, 25—69).—Addition of calcium hydroxide, chlorine (as sodium chloride), iron (as acetate), and phosphoric acid (as calcium salt) to the food had no material effect on the sp. gr. of the milk, even the amount of total ash being hardly appreciably altered. The percentage of calcium in the ash and in the milk is raised both by calcium hydroxide and calcium phosphate, but the increase in the milk is very slight. Addition of as much sodium chloride as the cows can consume had a scarcely appreciable effect on the percentage of chlorine in the milk, which, however, independently of feeding, considerably increases as the period of lactation advances. The amount of phosphoric acid in milk is not affected by addition of calcium phosphate to the food, and there was no material increase in the iron after food containing iron acetate.

Both phosphoric acid and iron (especially the former), as well as calcium, acted unfavourably on the digestion of proteids, whilst sodium chloride increased the digestibility. N. H. J. M.

Calcium Phosphate as an Addition to Food. V. SCHENKE (*Landw. Versuchs-Stat.*, 1903, 58, 291—312).—Precipitated calcium phosphate should be employed. Steamed or degelatinised bone meal and bone ash are of very slight use for feeding, and crushed bones are almost useless. The results of various investigators are discussed and a bibliography is appended. N. H. J. M.

Production and Distribution of Nitrates in Cultivated Soils. F. H. KING and A. R. WHITSON (*Bied. Centr.*, 1903, 32, 434—444; from *Bull. Agric. Exper. Stat. Univ. Wisconsin*, 1902, No. 93).—The greatest production of nitrates in 20 inches of soil was in the upper 6 inches and the least in the lowest 4 inches. Nitrification is relatively vigorous at a depth of 12—16 inches.

When the surface soil contains relatively little nitrates, this is to be attributed to diminished rise of water caused by the rapid drying at the surface. The soil just below the surface is then richer in nitrates.

The results of experiments on the effect of ploughing on the amount of nitrates in the soil showed that the ploughed soil contained more nitrates than the undisturbed soil.

Lysimeter experiments are described in which the amounts of nitrates were estimated in the drainage and in the soil before and after growing maize. N. H. J. M.

Rendering Atmospheric Nitrogen available for Agriculture and Industry. FRANK (*Zeit. angew. Chem.*, 1903, 16, 536—539).—The author points out that the supply of ammonia for agricultural purposes is dependent on other industries, that the supply of Peruvian guano is well-nigh exhausted, and that that of Chili saltpetre cannot at the present rate of export last more than 30 to 40 years. It becomes therefore necessary to utilise the atmospheric nitrogen. The various methods proposed for the utilisation of nitrogen in the production of cyanides and ammonia are shortly reviewed.

The whole of the nitrogen of calcium cyanamide (compare Erlwein, this vol., i, 611) can be converted into ammonia by heating with water under high pressure ($\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$). It seemed probable, therefore, that calcium cyanamide (or "lime-nitrogen") might be used as a fertiliser. Experiments by Wagner and by Gerlach have proved this view to be correct. In the soil, the calcium cyanamide is decomposed and the ammonia formed is nitrified, and thus the nitrogen becomes available for plants.

Dicyanodiamide (compare Erlwein, *loc. cit.*) can be obtained from calcium cyanamide, and is useful in the synthesis of creatine and other carbamide derivatives. J. McC.

Action of Different Crude Phosphates on Peat and other Soils. BRUNO TACKE (*Bied. Centr.*, 1903, 32, 445—448; from *Mitt. Ver. Förd. Moorkultur.*, 1902, No. 23, 312).—Algerian phosphate, "agricultural phosphate," and similar manures should not be applied to non-acid soils. N. H. J. M.

To what extent is Potassium Perchlorate a Plant Poison? MARTIN ULLMANN (*Bied. Centr.*, 1903, 32, 458—459; from *Die Regelung d. Verkehrs mit Chilisalpeter*, 1901).—The results of experiments with different plants showed that potassium perchlorate is a violent poison, but that it does not affect all plants equally, being especially injurious to grain crops. A grain crop may suffer considerably from the after effect of perchlorate applied in sodium nitrate to a previous crop. N. H. J. M.

Injuriousness of Perchlorate. T. DIETRICH (*Bied. Centr.*, 1903, 32, 461—463; from *Jahresber. Landw. Versuchs-Stat. Marburg*, 1901—1902).—The results of experiments with oats and mustard showed that the injury due to perchlorate diminished when the perchlorate was applied late. In the case of oats, the same amount of perchlorate which destroyed most of the plants at the end of July was without effect when applied in the middle of August. N. H. J. M.

Analytical Chemistry.

Gravimetric Analysis of Minute Quantities of Material. WALTHER NERNST and E. H. RIESENFELD (*Ber.*, 1903, 36, 2086—2093).—A micro-balance with torsional control is described, having a sensitiveness of 0.0380 mg. per scale division, and capable of being read to $\frac{1}{20}$ division. The tiny scale-pan is made of platinum and weighs 20 mg.; the analyses are carried out in this pan. Three analyses are given of calcite, the quantity used in each case being 2.5 mg.; the values found were $\text{CO}_2 = 43.80, 43.66, \text{ and } 43.81$, theory 43.96. Similarly, two analyses of yttrium sulphate by ignition of a single milligram gave the atomic weight as 88.0 and 87.8, theory 89. Traces of yttrium, erbium, and ytterbium chlorides were fractionally distilled by this method in a platinum tube heated in an electric furnace, but analysis by the method described showed that no separation had been effected. T. M. L.

Detection of Bromine in Urine. ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1903, 38, 157—164).—The usual method for the detection of bromine, namely, addition of sodium carbonate and potassium nitrate, evaporation, and ignition, and subsequent solution in water, addition of hydrochloric acid and chlorine water, and shaking with chloroform, cannot be employed when appreciable amounts of nitrites are formed, as a yellow coloration is also given by these. The yellow colour produced by nitrites may be removed by washing with water. It has also been found that the yellow colour produced when a nitrite and bromide are both present is removed by washing with water. If only a relatively small amount of nitrite (equal

volumes of 1 per cent. nitrite and bromide solutions) is employed, a permanent yellow coloration is produced, but not nearly so deep as when no nitrite is present.

It is advisable to leave out the nitrate and merely to add the carbonate, evaporate, ignite, extract with water, and test in the usual manner. The bromine may be confirmed by the liberation of iodine from potassium iodide solution.

Normal urine appears not to contain bromides. No general method for the detection of bromides in the presence of organic bromo-derivatives can be given.

J. J. S.

Detection of Bromine and Iodine in Urine. PROWAN CATHCART (*Zeit. physiol. Chem.*, 1903, 38, 165—169. Compare Sticker, *Zeit. Klin. Med.*, 1903, 45, and Salkowski, preceding abstract).—The author recommends carbon disulphide in preference to chloroform for the extraction of the bromine in Salkowski's method.

When iodides and bromides are both present, it is advisable to add light petroleum as well as carbon disulphide, when the characteristic violet- or rose-coloured solution is obtained floating on the water, provided too much chlorine has not been employed. Bromides alone do not colour the carbon disulphide—light petroleum mixture.

Iodine and bromine may be detected in 5 c.c. of urine containing 0.0125 per cent. of potassium bromide and 0.005 of potassium iodide by this method.

Jolles' method (*Abstr.*, 1898, ii, 637) gives good results when a fair amount of bromide is present, and so does the Carnot-Baubigny method (*Compt. rend.*, 1898, 126, 181).

J. J. S.

Estimation of Sulphur in Coals, Petroleums, Bitumens, and Organic Substances. FRITZ VON KONEK (*Zeit. angew. Chem.*, 1903, 16, 516—520).—The author's process is based on the fact that on applying Parr's calorimetric process (combustion in a bomb with sodium peroxide) the sulphur remains behind as sodium sulphate, which may then be estimated in the usual way.

When testing petroleum or similar liquids, it is advisable to cover the mixture with a little tartaric acid so as to ensure a successful combustion; in such a case, the experiment is, of course, useless for calorimetric purposes.

For minute details, the original article should be consulted. As a rather large amount of sodium peroxide is used and the percentage of sulphur in the coals is often but very small, the reagents must be carefully tested to ensure complete absence of sulphur compounds.

L. DE K.

Estimation of [Combined or Uncombined] Sulphuric Acid. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1903, 16, 617—619).—A modification of Müller's benzidine method (*Abstr.*, 1902, ii, 425).

The reagent is prepared by dissolving 18.5 grams of benzidine in 200 c.c. of *N*/10 hydrochloric acid and 1 litre of hot water; the liquid

is then filtered and diluted to 10 litres. One hundred and fifty c.c. of this liquid are added for each 0.1 gram of sulphuric acid supposed to be present. The precipitate is collected after 5 minutes, slightly washed with water, and then placed with the filter into a stoppered Erlenmeyer flask, 50 c.c. of water are added, and the whole violently shaken. The sulphuric acid is now titrated with *N*/10 alkali, using phenolphthalein as indicator; as soon as the bulk of the acid is neutralised, the liquid is heated to 50° and the titration continued. Finally, to make sure that no trace of benzidine sulphate has escaped the reaction, the liquid is heated to boiling and, if necessary, more alkali added.

Ferric sulphate cannot be titrated in this manner unless the iron is first removed, but for other sulphates the process is sufficiently accurate for technical purposes. L. DE K.

Detection of Thiosulphates in Foods in the Presence of Sulphites. CARL ARNOLD and CURT MENTZEL (*Zeit. Nahr. Genussm.*, 1903, 6, 550—551).—From 10 to 12 grams of the food (finely minced meat, butter, margarine, &c.) are heated on a water-bath with 10 c.c. of a mixture of equal parts of alcohol and water. After cooling and filtering, 2 to 3 c.c. of the clear filtrate are treated with 1 to 2 c.c. of sodium amalgam containing 0.5 per cent. of sodium. The action is allowed to proceed for 10 minutes, and then 2 to 3 drops of a 2 per cent. solution of sodium nitroprusside are added. The presence of 1 gram of sodium thiosulphate in 10 lbs. of food causes a red coloration to be produced. The simultaneous presence of sodium sulphite in the usual proportion used for preserving purposes (under 3 per cent.) does not interfere with the test, but very strong solutions of sulphite give a coloration when treated according to this test. W. P. S.

Volumetric Estimation of Nitric Acid. DÉBOURDEAUX (*Compt. rend.*, 1903, 136, 1668—1669).—Pelouze's method of estimating nitric acid is inconvenient and subject to serious errors. The author proposes a method which depends on the action of nitric acid on oxalic acid, the quantity of oxalic acid decomposed being determined by titration with potassium permanganate. The process is carried out in sulphuric acid solution, and so long as the concentration of the sulphuric acid does not exceed 20 per cent., no oxalic acid is destroyed by this. Manganese sulphate is used as a catalytic agent, and if the solution contains 20 c.c. of concentrated sulphuric acid per 100 c.c., the reaction takes place according to the equation: $3\text{H}_2\text{C}_2\text{O}_4 + 2\text{KNO}_3 + \text{H}_2\text{SO}_4 = 4\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + 6\text{CO}_2 + 2\text{NO}$. If the concentration of the sulphuric acid be lower, the reaction is: $4\text{H}_2\text{C}_2\text{O}_4 + 2\text{KNO}_3 + \text{H}_2\text{SO}_4 = 5\text{H}_2\text{O} + \text{K}_2\text{SO}_4 + 8\text{CO}_2 + \text{N}_2\text{O}$. In carrying out the estimation, the solution should contain 4 to 6 grams of manganous sulphate and 11 to 14 c.c. of sulphuric acid per 100 c.c., and the solution should be slowly heated to 94°.

When substances are present which reduce permanganate, the oxalic acid is estimated by precipitation as calcium oxalate, which may be either weighed or estimated volumetrically. J. McC.

Applicability of Schloësing's Method to the Estimation of the Nitrogen in Nitrates in Presence of Organic Substances. PAUL LIECHT and ERNST RITTER (*Zeit. anal. Chem.*, 1903, 42, 205—232).—In view of the adverse opinion which has been expressed by some analysts (compare Pfeiffer and Thurmann, *Abstr.*, 1895, ii, 369) respecting the accuracy of Schloësing's method when applied to the estimation of nitrates in urine and other excrementitious manurial materials, the authors have submitted the method to a fresh examination with the special object of ascertaining whether its results could be trusted under these conditions, as well as of studying the question whether the various forms of the method which have been proposed (measurement of the nitric oxide, oxidation to nitric acid and titration, absorption by ferrous sulphate) give concordant numbers.

In common with Warington (*Trans.*, 1880, 37, 468; 1882, 41, 345) and others, they advocate the use of an evolution apparatus of the smallest convenient size, and the collection of the gas over mercury. The other methods of ascertaining the amount of the nitric oxide produced were found to be less exact. Where the nitrate is largely contaminated with organic and inorganic impurities, the solution in which it is contained should first be introduced into the flask and boiled to expel the air, but when the nitrate is relatively pure, the acid ferrous chloride should be first introduced. They strongly support the proposal that the boiling should be interrupted when near the end of the decomposition, the gas tube clamped, and the flask cooled. The diminution of tension in the flask greatly promotes the expulsion of the last traces of nitric oxide from the liquid. The gas collected in their experiments was treated with a little potassium hydroxide solution in a Hempel's pipette, and the residual gas was proved to consist of nitric oxide by absorbing it with an alkaline solution of sodium sulphite (*Divers*, *Trans.*, 1899, 75, 82). In no case was the absorption absolutely complete, but the residue was as a rule less than 0.1 c.c., and was therefore negligible.

Experiments with pure potassium nitrate (1 to 25 mg.) gave results ranging from 97 to 98.9 per cent. of the nitrogen taken.

Applying the principles thus ascertained, experiments were made in which large amounts of ammonium sulphate, urea, human and bovine urine, drainage from manure heaps, and horse-dung were mixed with quantities of nitrate containing amounts of nitrogen varying from 1 to 40 mg. The results ranged from 93 to 97.5 per cent. In no case was any foreign gas other than carbon dioxide found. When working with urine, &c., a difficulty was encountered due to the obstinate frothing of the contents of the reaction flask. This was avoided by first evaporating the liquid, then precipitating with lead acetate, freeing the filtrate from lead by ammonia, and again evaporating. The heating of the reacting mixture must be pushed until no liquid remains in the flask; bumping, which occurs towards the end, may be prevented by the use of pumice, and it is advisable to introduce a small quantity of boiled potassium hydroxide solution into the collecting vessel, since, in some cases, benzoic acid distils over with the gas and crystallises in the upper part of the tube.

Cows' urine, horse-dung, and the drainage from manure heaps were

found to be absolutely free from nitrates. Nitrates are, however, present in fresh human urine.
M. J. S.

Behaviour of Nitrous Acid towards Methyl-orange. GEORG LUNGE (*Zeit. angew. Chem.*, 1903, 16, 509—511).—It has been stated that nitrous acid is inert towards methyl-orange. The author finds that this phenomenon is due to the fact that nitrous acid destroys this colouring matter. If, however, this is prevented by having the solution very dilute, operating as quickly as possible, and not adding the methyl-orange until the liquid is nearly neutralised, nitrous acid may be accurately titrated with this indicator.
L. DE K.

Analysis of Wiborgh Phosphate and Basic Slag. MATS WEIBULL (*Landw. Versuchs-Stat.*, 1903, 58, 263—274).—The direct method for phosphoric acid as used for basic slag was found to be unsuitable in the case of Wiborgh phosphate owing to the precipitation of silica. This, however, can be avoided by adding a suitable amount of ferric chloride (about 0.1 gram of iron to 0.5 gram of Wiborgh phosphate).

Basic slag which contains large amounts of silica also gives high results by the direct method as compared with the molybdenum method. Correct results are obtained by the direct method when ferric chloride is added. As it is sometimes doubtful whether citric acid extracts of basic slag contain sufficient iron, it is desirable to always add ferric chloride.
N. H. J. M.

Quantitative Deposition of Metals by Electrolysis. P. DENSO (*Zeit. Elektrochem.*, 1903, 9, 463—470).—The smallest *E.M.F.*'s which will decompose normal solutions of the sulphates of zinc, cadmium, nickel, and copper are 2.54, 2.24, 2.09, and 1.48 volts respectively. The author shows that copper may be separated quantitatively from solutions containing the other metals mentioned when one accumulator cell (with the *E.M.F.* of 2 volts) is used as the source of current. The deposition requires about 8 hours under ordinary circumstances, but this may be much reduced (to 3 hours for 0.25 gram of copper) by stirring, by platinising the anode, and by making the solution acid. The stirring is conveniently done by attaching the cathode to the hammer of an electric bell.

Separation of Copper and Nickel.—The solution used is acidified with sulphuric acid to about *N/5* strength. The copper is first deposited, using one accumulator cell, after which the acid is neutralised with sodium carbonate and the electrolysis continued with two accumulator cells in order to deposit the nickel.

The separation of copper and cadmium is carried out in the same way, with the difference that it is not necessary to neutralise the acid after the copper is deposited, since cadmium is deposited quantitatively from acid solution when two accumulator cells are used.

Cadmium and zinc are very easily separated, even when a large excess of the latter metal is present; two accumulator cells are used, and the solution is made fairly strongly acid (up to normal). The zinc may be subsequently deposited from solution in potassium cyanide.

The analyses given as examples of the methods are very satisfactory.

T. E.

Use of Lead Dioxide in Analysis. STEFAN BOGDAN (*Bull. Soc. chim.*, 1903, [iii], 29, 594—597).—When precipitating the metals of the zinc group with ammonium sulphide, it is desirable to free the filtrate from the excess of that reagent; this may be conveniently effected by digesting the liquid for a few minutes with an excess of lead dioxide.

Calcium, strontium, and barium are not affected by this process.

L. DE K.

Separation of Manganese and Iron. MAX DITTRICH (*Ber.*, 1903, 36, 2330—2333).—The method is based on Jannasch's separation of zinc, cobalt, and nickel from manganese by means of potassium cyanide and hydrogen peroxide (*Abstr.*, 1892, 240). It is first necessary to reduce all the iron present to the ferrous form; potassium cyanide then converts it into potassium ferrocyanide, and part of the manganese into a similar compound. The addition of sodium hydroxide does not affect the iron salt, but converts the manganese compound into manganous hydroxide. As this is not easily filtered, it is best to convert it into peroxide by the addition of 3 per cent. hydrogen peroxide, when, after dilution with hot water and remaining for 15 minutes, it is easily filtered. All the manganese is now present in the precipitate and all the iron in the filtrate. The former is determined as Mn_3O_4 by precipitation with ammonia in presence of hydrogen peroxide; for the latter, the method described by Dittrich and Hassel (*Abstr.*, 1903, ii, 254), using persulphates in acid solution, is advised.

E. F. A.

Estimation of Vanadium in Alloys. PAUL NICOLARDOT (*Compt. rend.*, 1903, 136, 1548—1551).—An attempt to estimate vanadium in alloys of iron by oxidising it to vanadic acid and dissolving out with ammonia (*Abstr.*, 1902, i, 22) showed that this method cannot be made use of on account of the sparing solubility of the vanadic acid.

When an alloy of iron and vanadium is dissolved in acid in such a way that no oxidation can take place, the iron dissolves, but the vanadium remains completely insoluble, and may be estimated in this way. Just sufficient hydrochloric acid is used to effect complete solution of the iron; the residue is collected, dried in a platinum crucible, and gently ignited with hydrofluoric acid until the silicon is expelled. The residual vanadium is heated at 350° and weighed as vanadic oxide.

J. McC.

Separation of Gold and Platinum. RICHARD WILLSTÄTTER (*Ber.*, 1903, 36, 1830).—Gold chloride is easily soluble in ether, whilst platinum chloride is insoluble. Gold and platinum can be separated quantitatively from an aqueous solution containing the mixed chlorides by simply extracting with ether.

A. McC.

Qualitative and Quantitative Analysis of Iridium Osmides. ÉMILE LEIDJÉ and QUENNESSEN (*Compt. rend.*, 1903, 136, 1399—1401. Compare *Abstr.*, 1901, ii, 62, 695; 1902, ii, 360; this vol., ii, 24).—The iridium osmide in a finely divided condition is intimately mixed

with four times its weight of sodium peroxide, and the mixture added in small portions at a time to sodium hydroxide fused in a nickel dish. The mass is treated with water, and the residue washed with sodium hypochlorite solution. The liquid contains all the osmium and ruthenium in the form of osmate and ruthenate, and some of the iridium as iridate. The liquid is distilled in a current of chlorine at 70° into a solution of alkali; the osmium and ruthenium distil as peroxides, but the iridium is retained by the alkaline solution. The distillate is again distilled, this time in a current of air, into a three-bulb condenser, the first bulb of which contains hydrochloric acid and the other two sodium hydroxide solution to which 2 per cent. of alcohol has been added. The hydrochloric acid retains the ruthenium, but the osmium passes this and condenses in the alkaline solution.

The osmium is precipitated from the solution by means of aluminium; it is filtered, dried, ignited in hydrogen, and weighed as metal. The solution containing the ruthenium is evaporated to get rid of excess of acid, then dissolved in water, and the metal precipitated by magnesium. The metal is treated in the same way as osmium.

The residue from the first distillation is acidified with hydrochloric acid, and the residue from the fusion is dissolved in it. The foreign metals present are separated by the usual procedure, and the iridium is converted into the double nitrite by the addition of sodium nitrite and sodium carbonate. The solution is filtered, and the iridium converted into iridichloride by hydrochloric acid. A current of hydrogen chloride is passed into solution, and nearly all the sodium chloride is precipitated. After filtering, the solution is evaporated to get rid of the acid, and the iridium is then precipitated as metal by means of magnesium, and treated as for osmium.

J. McC.

Estimation of the Nitrogenous Constituents in Sea Water, with remarks on Colorimetric Methods. H. CHRISTIAN GEELMUYDEN (*Zeit. anal. Chem.*, 1903, 42, 276—292).—As a first step in the solution of the question as to the proximate source of the nitrogenous nutriment of marine vegetation, the author has investigated methods for the estimation of ammonia, nitric and nitrous acids in sea water.

Nitrous Acid.—Griess's reagent (α -naphthylamine and aniline-*p*-sulphonic acid in acetic acid solution) was employed colorimetrically. Since it was found that the other constituents of sea water modified the Griess reaction, causing the colour to be more intense than in distilled water, it was necessary to devise a method in which the standard should be prepared from the same specimen of water as that under examination. Two equal portions, *A* and *B*, of the water were taken. To *B*, a measured volume of a nitrite solution of known strength was added. Both were then treated with equal volumes of acetic acid and Griess's reagent, and by examination in a Wolff's colorimeter the length of the column of *B*, which gave the same intensity of colour as a standard length of *A*, was ascertained. From this, the unknown amount (*C* in hundredths of a milligram per litre) of nitrous acid in

A can be calculated by the equation $C = \frac{1000}{S} \cdot \frac{nH_2}{kH_1 - H_2}$, in which S is the original volume of A (in c.c.), n the weight of N_2O_3 (in 0.01 mg.) added to B . H_1 is the length of column of A , and H_2 that of B , which give equal colours, and K is the ratio S_2/S_1 of the volumes of the two specimens after adding the reagent. If the volume of nitrite solution added to B is small compared with S , K may be neglected, or if an equal volume of distilled water be added to A , it disappears. The mixtures should be allowed to remain at least 24 hours before observation. By test estimations, it was found that the method gave a fair approximation when the quantity of N_2O_3 did not exceed 0.5 mg. per litre, and when the amount (n) of added N_2O_3 was kept as small as possible; 1 c.c. of nitrite solution containing 0.01 mg. of N_2O_3 is sufficient to add to 150 c.c. of water. With stronger solutions, the red colour has a yellow tone which, on keeping, augments at the expense of the red. A form of colorimeter is also described in which the above principle can be applied to coloured liquids such as urine.

Estimations of nitrous acid in water from the Christiania Fiord showed quantities of N_2O_3 varying from 0.014 to 1.206 mg. per litre. Uncontaminated sea water, however, rarely gives any colour with Griess's reagent.

Nitric Acid.—Attempts to employ the diphenylamine test were partially successful, but nitrates are seldom to be detected in sea water even by that sensitive test.

Ammonia.—The distillation of the water with an alkali hydroxide and the application of Nessler's reaction showed amounts of ammonia varying from 0.028 to 0.19 mg. per litre, but the author regards it as probable that part of this may have been derived from nitrogenous substances other than ammonium salts. This inquiry was not followed up.

M. J. S.

Estimation of Methyl attached to Nitrogen. GUIDO GOLDSCHMIEDT and O. HÖNIGSCHMID (*Ber.*, 1903, 36, 1850—1854).—Compounds which contain carbonyl attached to the carbon situated in the ortho-position to the nitrogen, such as, for instance, the methylbetaine of papaverinic acid, apparently give up a portion of the methyl group attached to this nitrogen as methyl iodide when heated with hydriodic acid in the Zeisel methoxyl determination. Values for methoxyl in excess of the real are obtained, thus the methylbetaine of quinolinic acid, which contains no methoxyl group, gave a value of 5—6 per cent. This explains the high values 10—12 per cent. instead of 8 per cent. previously obtained in the case of papaverinic acid (*Abstr.*, 1897, i, 131). Recently Busch has obtained similar results for compounds containing the grouping $\begin{smallmatrix} \text{CO} \\ \cdot \\ \text{CO} \end{smallmatrix} > \text{N} \cdot \text{NMe} \cdot$ (*Abstr.*, 1902, i, 501).

E. F. A.

Estimation of Eugenol in Oil of Cloves. EDWARD C. SPURGE (*Pharm. J.*, 1903, [iv], 16, 701—702, and 757—758).—The results are given of comparative estimations of eugenol by the methods of Verley

and Bölsing (compare Abstr., 1902, ii, 54), Umney, and Thoms (Abstr., 1892, 250). As oil of cloves contains considerable quantities of eugenol as ester (from 7 to 17 per cent. calculated as eugenyl acetate), none of the methods gave strictly accurate results. Verley and Bölsing's method *plus* the eugenol obtained by saponification yielded the most accurate results, whilst Umney's method, uncorrected, gave figures sufficiently trustworthy for a pharmacopœial valuation of oil of cloves. Thoms' method is considered to be inaccurate and tedious.

W. P. S.

Detection of Peroxides in Ether. ARMAND JORISSEN (*Ann. Chim. anal.*, 1903, 8, 201—202).—In a small porcelain capsule are placed 0.1 gram of powdered vanadic acid and 2 c.c. of sulphuric acid, the whole is heated for 10—15 minutes on the water-bath, and then allowed to cool. The mass is then dissolved in water and made up to 50 c.c.; 1 or 2 c.c. of this reagent are placed in a test-tube and 5 or 10 c.c. of the suspected ether are added, and the whole is well shaken. Should peroxides be present, the mixture assumes a colour varying from rose to blood-red.

L. DE K.

Detection of Lactose in Urines by means of Phenylhydrazine. CH. PORCHER (*Compt. rend. Soc. Biol.*, 1903, 55, 500—501).—The urine is clarified with lead acetate, phenylhydrazine and acetic acid are added, and the mixture heated for 1—1½ hours on the water-bath. When cold, the deposit (which has no striking microscopical appearance) is well washed with cold water and then recrystallised from boiling water. In the presence of lactose, needle-like crystals are obtained, which frequently occur in characteristic sphaerolitic aggregates.

L. DE K.

New Method of estimating Oxalic Acid in Urine and Alimentary Matters. JACQUES M. ALBAHARY (*Compt. rend.*, 1903, 136, 1681—1682).—To the urine of 24 hours, 50 c.c. of a 10 per cent. solution of sodium carbonate are added and the liquid evaporated on the water-bath to a third of its original volume. Twenty c.c. of a solution containing 10 per cent. of magnesium chloride and 20 per cent. of ammonium chloride are added and the liquid is shaken with animal charcoal. It is further concentrated on the water-bath for an hour, then after filtration the oxalic acid is precipitated with a solution of calcium chloride, and acetic acid is added until the liquid shows an acid reaction. The calcium oxalate is allowed to settle for 12 hours and is then estimated in the usual way. The magnesium solution removes the phosphates, and the mucilaginous matter, which would render filtration slow, is absorbed by the animal charcoal, which at the same time carries down all the uric acid.

The results obtained by this method are somewhat higher than those found by the methods of Salkowski and of Autenrieth and Barth.

J. McC.

Halphen's Reaction with Coloured Butters. FRANZ UTZ (*Chem. Zeit.*, 1903, 27, [53], 675).—With regard to the possibility of

butters containing "butter colouring" (which is sometimes a solution of the colour in cotton-seed oil) yielding a coloration with Halphen's test indicating the presence of cotton-seed oil, the author has made a number of experiments and finds that butters so coloured give no reaction with Halphen's test. On adding such an amount of "butter colouring" as was sufficient to give a reaction with this test, the butter became unpalatable and, consequently, unsaleable.

W. P. S.

New Reactions for distinguishing Heated from Raw Milk and for the Detection of Hydrogen Peroxide in Milk. CARL ARNOLD and CURT MENTZEL (*Zeit. Nahr. Genussm.*, 1903, 6, 548—549).—On adding a drop of a freshly prepared 2—3 per cent. solution of *p*-diethyl-*p*-phenylenediamine in alcohol or acetone to 10 c.c. of raw milk containing 6 drops of hydrogen peroxide, a red coloration is obtained, gradually changing into violet. A saturated alcoholic solution of *p*-diaminodiphenylamine hydrochloride rendered feebly acid with hydrochloric acid gives a bluish-green coloration with raw milk containing hydrogen peroxide. These tests will detect less than 2 per cent. of raw milk in heated milk. The two substances mentioned above give the same colorations with chlorine, bromine, and nitric oxide, but only react with hydrogen peroxide in the presence of oxydase. 0.004 per cent. of hydrogen peroxide may be detected in raw or heated milk by these reagents. In the case of heated milk, however, about 15 per cent. of raw milk must be first added to supply the necessary oxydase.

W. P. S.

Reagent for Aldehydes. MANGET and MARION (*Ann. Chim. anal.*, 1903, 8, 207—208).—The aldehyde is dissolved in hot milk, or this is added to the aldehyde already in solution. A few minute crystals of amidol are then sprinkled over the surface, when a yellow colour will appear. The reaction has proved successful with most of the aldehydes except valeraldehyde and dextrose.

L. DE K.

Estimation of Formaldehyde in Air. GYSBERT ROMYN and J. A. VOORTHUIS (*Bull. Soc. chim.*, 1903, [iii], 29, 540—543).—A known volume of air containing formaldehyde is passed through a Kyll tube in which a few c.c. of Nessler's solution have been placed. The mercury precipitated by the action of the formaldehyde is converted into mercuric iodide by the addition of a known quantity of iodine dissolved in solution of potassium iodide. The solution is then acidified with dilute hydrochloric acid and the excess of iodine added ascertained by titration with sodium thiosulphate solution. This process was described by Romeyer in a thesis published in 1902, but was not applied by this author to the estimation of formaldehyde in air. The method is more convenient than the iodometric process described by Peereboom (*Hyg. Rundschau*, 1893, No. 16), and gives results as accurate as those obtained by the latter method.

T. A. H.

New Method for the Analysis of Ferri- and Ferro-cyanides. MAX DITTRICH and C. HASSEL (*Ber.*, 1903, 36, 1929—1932).—The method is based on the decomposition of the complex cyanide by persulphates in the presence of mineral acid. 0.5 gram of the cyanide is dissolved in 50 c.c. of water containing 5 drops of dilute sulphuric acid, 30 c.c. of a clear 10 per cent. ammonium persulphate solution is added, and the mixture warmed on the water-bath until it again becomes clear ($\frac{1}{2}$ — $\frac{3}{4}$ hour). It is not advisable to heat over a free flame, and it is absolutely essential that free acid should be present. Concentrated hydrochloric acid is added and the iron precipitated as ferric hydroxide in the usual manner. The gas evolved contains hydrogen cyanide, the amount being some 50 per cent. of the theoretical. Small amounts of ammonium salts are also formed. Ferri-cyanides can be estimated in exactly the same manner. In the analysis of Berlin blue it is advisable to boil with alkali before oxidising with the persulphate.

J. J. S.

Estimation of Urea; a New Ureometer. G. SELLIER (*Ann. Chim. anal.*, 1903, 8, 210—212).—The instrument consists of a graduated burette, to the top of which is attached a specially constructed apparatus, for which the drawing in the original article should be consulted; the burette is plunged into a reservoir containing water.

The urine, to which a little dextrose is added, is placed in one compartment of the apparatus, whilst in the other is placed an alkaline solution of sodium hypobromite. On being rotated, the liquids are made to mix, and the nitrogen evolved passes into the burette, where it is measured with the usual precautions.

L. DE K.

Estimation of Urea. G. DONZÉ and EUGÈNE LAMBLING (*Compt. rend. Soc. Biol.*, 1903, 55, 539—542).—A criticism of Sallerin's experiments, who, whilst accepting Folin's method as a standard process, states that the process introduced by Yvon gives results which are too high with original urines and too low with samples purified by means of phosphotungstic acid.

The authors state that Sallerin has used too concentrated a solution of phosphotungstic acid (23 per cent.), which then also precipitates a portion of the urea. A 10 per cent. solution presents no such danger. On the whole, Yvon's process is satisfactory.

L. DE K.

Estimation of Urea in Human Urine. FRANZ EREEN (*Zeit. physiol. Chem.*, 1903, 38, 544—551).—The Liebig-Pflüger, Mörner-Sjöquist, Schöndorff, and Moor methods of estimating urea were compared. That of Schöndorff was found to give the best results.

W. D. H.

Precipitation of Some Alkaloids by Uranium Nitrate. Reaction for Morphine. JULES ALOY (*Bull. Soc. chim.*, 1903, [iii], 29, 610—611).—The alkaloids, with the exception of morphine, caffeine, theobromine, and asparagine, are precipitated by adding to their aqueous, ethereal, or alcoholic solutions a neutral solution of

uranic nitrate. The alkaloids may be recovered from the precipitates by treating them with sodium hydrogen carbonate. The precipitates, which are more or less dark yellow in colour, are amorphous at first, but several soon become crystalline.

Morphine, however, is the only alkaloid which exerts a reducing action on the uranium compound, and causes a fine red coloration; this reaction the author recommends as a very delicate test for its presence in a mixture of alkaloids.

L. DE K.

Analyses of Hexone Bases. ALBRECHT KOSSEL and A. J. PATTEN (*Zeit. physiol. Chem.*, 1903, 38, 39—45. Compare Kossel and Kutscher, *Abstr.*, 1901, i, 107).—Histidine may be separated from arginine, aspartic acid, and the other decomposition products of proteids by means of mercuric sulphate. The authors recommend the original method for the separation of histidine and arginine, but the new method for the purification of the histidine so obtained.

J. J. S.

Action of Iodine on Nicotine. CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1903, 42, 232—276).—At the ordinary temperature, the action of iodine on nicotine in ether or chloroform solution results in the replacement of hydrogen by iodine and the formation of periodine compounds which are insoluble in the menstruum. The composition of these products is influenced by the relative amounts of iodine and nicotine present, as well as by the proportion of the solvent, and as these conditions are continuously varying throughout the period of reaction, various periodides of both iodonicotine hydriodide and of nicotine hydriodide are precipitated. Basic compounds are at the same time obtained. The results tend to support the evidence already obtained by the titration of nicotine with acids in presence of a variety of indicators, that this alkaloid normally functions as a mon-acid base. As the ordinary methods of analysing these substances are inapplicable, the following scheme was devised. *Estimation of attached iodine.*—The substance is dissolved in alcohol containing at least five times as much concentrated sulphuric acid as would be required to convert the nicotine into sulphate; the free iodine is then titrated by thiosulphate. *Estimation of the hydriodic acid.*—The substance is dissolved in a mixture of alcohol, sulphuric acid, and acetone, sulphurous acid is immediately added to convert the free iodine into hydriodic acid, and this is then precipitated by adding a solution of silver sulphate in acidified alcohol. The precipitate is washed first with cold alcohol containing sulphuric acid, then with warm dilute sulphuric acid, and finally with hot dilute nitric acid. The amount of attached iodine is deducted from that found. *Estimation of the total iodine.*—Carius's method is employed. Various alternative methods are also described.

When iodine (1 atom) acts on nicotine (1 mol.) in ethereal solution, the principal product is the periodide, $2(\text{C}_{10}\text{H}_{14}\text{N}_2)\text{HI}, \text{I}_2$, with traces of $\text{C}_{10}\text{H}_{14}\text{N}_2\text{HI}, \text{I}_{1-2}$ and $2(\text{C}_{10}\text{H}_{14}\text{N}_2)\text{HI}, \text{I}_3$; whilst about one-tenth of the nicotine is iodised to the compound $\text{C}_{10}\text{H}_{13}\text{IN}_2$. With more iodine (2 atoms), especially at a low temperature, the product

is chiefly the periodide, $(C_{10}H_{13}IN_2, C_{10}H_{14}N_2)HI, I_4, xCHCl_3$, whilst with still larger proportions of iodine the periodide, $C_{10}H_{14}N_2, HI, I_2$ (m. p. 123°), is predominant. The same compound is obtained in a practically pure state when the calculated amounts of nicotine, hydriodic acid, and iodine are dissolved in chloroform containing 10 vols. per cent. of alcohol, and also when iodine (4 atoms) reacts with nicotine (1 mol.) in ether mixed with $1/20$ of alcohol. It forms brownish-red to blackish-brown, lustrous crystals, insoluble in water, slightly soluble in acidified water, fairly soluble in alcohol, especially when acidified, and freely soluble in acetone. Although Wertheim and Huber have described this compound, their method of preparation cannot have yielded it in the pure state.

Attempts to obtain the gold-bronze moniodo-nicotine salt in a pure state, by the direct action of iodine on nicotine, were not successful.

M. J. S.

Assay of Opium. EUGÈNE LÉGER (*J. Pharm. Chim.*, 1903, [vi], 17, 553—560).—A review of methods for the estimation of morphine in opium. A modified form of Loof's process is finally recommended.

Six grams of the dried sample are mixed with 48 c.c. of a 2 per cent. solution of sodium salicylate and shaken for 5 minutes. After waiting for an hour, the mass is squeezed in a cloth and the liquid filtered. Thirty-six c.c. of the filtrate are then put into a stoppered bottle and mixed with 4 c.c. of ether and 1 gram of officinal ammonia. After 24 hours, the liquid is passed through a double filter, and the morphine is then also brought on to the filter by three successive washings with 8 c.c. of water. After drying at 100° , the morphine is washed three times with 8 c.c. of benzene and then again dried at 100° before weighing. As excess of ammonia cannot be avoided, this and similar methods must be attended by a slight loss.

L. DE K.

Estimation of Purin Compounds, Uric Acid, and Alloxuric Bases in Urine by a Combination of the Processes of Folin, and Schaffer and Denigès. LÉON GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 643—644).—The reagent is made, according to Folin-Schaffer, by dissolving 500 grams of ammonium sulphate and 5 grams of uranium acetate in 650 grams of water and 60 grams of 10 per cent. acetic acid.

Three hundred c.c. of the urine, freed, if necessary, from albumin, are mixed with 75 c.c. of the reagent, and after 5 minutes the whole is thrown on to a large filter. In 100 c.c. of the filtrate, the purin substances are estimated by Denigès's silver method and the result is multiplied by 1.25. Another 125 c.c. of the filtrate are mixed with 5 c.c. of ammonia; after 12 hours, the uric acid is collected, washed with solution of ammonium sulphate, and redissolved in solution of sodium hydroxide, which is then further treated by Denigès's silver process.

The difference between the two titrations represents the alloxuric bases.

L. DE K.

The Reaction of Reduced Crystal-violet. HENRI CAUSSE (*Compt. rend.*, 1903, 136, 1269—1270. Compare Abstr., 1901, ii, 581).—In a solution containing oxygen and the hydrochloride of crystal-violet reduced and rendered colourless by sulphurous acid, the oxygen is absorbed by the leuco-salt, and the product in its turn is reduced by the sulphurous acid with formation of sulphuric acid.

Comparative results obtained with distilled water and with tap-water to which various reagents were added, show that the presence of a small quantity of alkali or alkaline-earth carbonate renders the test more active. J. McC.

Oxidation of Proteids by Jolles's Method. EUGEN LANZER (*Zeit. Natur. Genussm.*, 1903, 6, 385—396).—The following results were obtained on treating various proteids according to this method (compare Abstr., 1901, i, 490). The figures show the percentages of nitrogen in the oxidised proteid as (1) carbamide; (2) substances precipitated by phosphotungstic acid; and (3) total nitrogen in the proteid.

	(1)	(2)	(3)
Amorphous serum-albumin.....	11.56	3.01	14.64
Casein	11.34	3.44	15.73
Fibrin	7.81	4.26	16.64

These results agree well with those obtained by Jolles. Schultz's unfavourable results (compare Abstr., 1901, i, 780) are considered to be due to his having altered the method in its most essential parts.

W. P. S.

Estimation of Casein Precipitated by Rennet. HENRY D. RICHMOND (*Analyst*, 1903, 28, 138—140).—The amount of curd separated from milk by rennet may be calculated from the formula:

$$c = [100(D_M - D_W)] / [D_M(1 - KD_W)], \text{ in which } K = 1/d,$$

where c = percentage by weight of curd, D_M = sp. gr. of the milk, D_W = sp. gr. of the whey, and d = sp. gr. of the curd. $K = 0.71$ as deduced from the results of experiments. For calculating the specific gravity of the milk free from fat, in order to eliminate the influence of the latter, the following formula may be used:

$$D_s = [(100 - f)D_M] / [100 - (fD_M/0.93)],$$

where D_s = sp. gr. of the milk minus fat, D_M = sp. gr. of the milk, and f = percentage by weight of the fat.

A simple approximation formula which gives fair results is:

$$c = \{G_M + f_M - (G_W + f_W)\} \times 0.35,$$

in which c = percentage of curd by weight, G_M = lactometer degrees of milk, G_W = lactometer degrees of whey, f_M = percentage of fat in the milk, and f_W = percentage of fat in the whey. The curd estimated by this method does not agree with the proteid precipitated, but with the proteid *plus* mineral matter, the latter being about 10 per cent. of the curd, neither do the results represent the actual casein in the milk.

W. P. S.

General and Physical Chemistry.

Influence of Temperature on the Dichroism of Mixed Liquids, and Verification of the Law of Indices. GEORGES MESLIN (*Compt. rend.*, 1903, 137, 182—184. Compare this vol., ii, 521).—In mixed liquids which show spontaneous dichroism if the two substances (solid and liquid) have indices of refraction which are altered to different extents by rise of temperature, this effect should be apparent in the dichroism. The temperature coefficients of potassium sulphate and benzene are very different; at 20°, that of benzene is the higher, whilst at 60° it is the lower. At 20°, this mixture is positively dichroic, but negatively so at 60°. Sodium borate and turpentine, nickel sulphate and benzene, and nickel sulphate and toluene are negatively dichroic at 20°, and positively at 60°. When the difference in the indices does not exceed 0.02, only a decrease of the dichroism takes place, and there is no inversion. At 20°, zinc sulphate and benzene, zinc sulphate and toluene, and potassium chlorate and benzene are positively dichroic, and at 60° they are still positive, but much weaker. The ferrous sulphate and toluene mixture loses its dichroism at 60°.

Precisely the same effects are to be observed with magnetic dichroic liquids. This temperature influence is important because it leads to the detection of dichroism in some cases where, at a particular temperature, such was not apparent; thus, at 20°, a mixture of potassium carbonate and turpentine is inactive, but becomes positively dichroic at 60°.

J. McC.

The Electromotive Force of the Daniell Cell. J. W. COMMELIN and ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 4—11).—The authors criticise the conclusions of Chaudier (*Abstr.*, 1902, ii, 239) and show that these are based on erroneous results. They do not find, as Chaudier claims to have found, that the *E.M.F.* has a maximum value when the zinc sulphate solution contains 0.5 gram of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ to 100 c.c. of water. The *E.M.F.* was determined in a specially constructed cell in which all diffusion of copper salt solution to the zinc electrode was avoided. The zinc electrode was an amalgam of 9 parts of mercury and one part of zinc; as copper electrode, a thick copper wire was employed, and it was electrolytically covered with copper immediately before use. A saturated solution of copper sulphate was used; this contains 19.25 grams of anhydrous copper sulphate in 100 grams of water at 15°. A saturated solution of zinc sulphate at 15° contains 150.56 grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ per 100 c.c. of water. The *E.M.F.* was measured when solutions of varying strength of zinc sulphate were used. When the solution contains 1/12 gram of crystallised zinc sulphate to 100 c.c. of water, the *E.M.F.* is 1.146 volts; with a solution of 1 gram of the salt to 100 c.c. of water, it is 1.131, and with a saturated solution it is 1.081. The progressive change of the values is in harmony with Nernst's equation, according to which the *E.M.F.* must decrease as the concentration of the zinc sulphate increases.

J. McC.

Thallium Accumulator. LESLIE JONAS (*Zeit. Elektrochem.*, 1903, 9, 523—530).—When a solution of thallous hydroxide is electrolysed, thallium is deposited on the cathode and an oxide on the anode. The oxide contains slightly less oxygen than is required by the formula Tl_2O_3 , its composition being better represented by $17Tl_2O_3, Tl_2O$. The quantity deposited is equal to that calculated by means of Faraday's law. The process is reversed when the direction of the current is reversed. The chemical reaction in the cell $Tl_2O_3 | TlOH' | Tl$ is, therefore, $Tl_2O_3 + 4Tl + 3H_2O \rightleftharpoons 6Tl' + 6OH'$, and the *E.M.F.* is given by $\pi = \pi_0 - RT/4F \log C_{Tl}^0/C_{OH}^0$. By means of this formula, the difference between the *E.M.F.* of two cells containing solutions of different concentrations may be calculated. The author's experimental results agree satisfactorily with the calculation. The *E.M.F.* of the cells used lie between 0.55 and 0.65 volt, and the capacity per kilogram is no greater than that of the lead accumulator. T. E.

Electromotive Behaviour of the Oxides of Cerium. EMIL BAUR and A. GLAESSNER (*Zeit. Elektrochem.*, 1903, 9, 534—539).—Measurements of the *P.D.* between platinum electrodes and solutions containing cerous and ceric sulphates and nitrates in various proportions are tabulated. From these, it appears that a cell in which one electrode is immersed in a solution of cerous salt and the other in a solution of a ceric salt would have an *E.M.F.* of about 0.6 to 0.7 volt, but that this would fall to about 0.1 volt when 10 per cent. of the ceric had been converted into cerous salt and *vice versa*. The differences between the potentials in alkaline solution are much smaller. A solution of ceric peroxide in 50 per cent. potassium carbonate solution gives about the same *P.D.* with a platinum electrode as an alkaline solution of a ceric salt. The action of reducing agents on alkaline solutions of ceric salts is extremely slow at the ordinary temperature, at 70° it is more rapid. Ammonia is oxidised to nitrogen, dextrose is partially oxidised to carbon dioxide, but the measurements of the *P.D.* between platinum and the ceric solutions containing the reducing agents show that equilibrium is not attained. Cells of the type Pt or $Ni | \text{cerous salt} + \text{reducing agent} | \text{ceric salt} + \text{oxygen} | C$ are then investigated, dextrose, hydrogen, and sawdust being the reducing agents used, and 50 per cent. potassium carbonate solution the electrolyte. When a current of 2 to 4 milliamperes is taken from the cells, the *E.M.F.* falls to a very small fraction of its original value. Sawdust has practically no depolarising effect, the result obtained with it being practically the same as that obtained with no depolariser. Hydrogen and dextrose give two or three times as much electrical energy per unit time. The velocity of reaction between the aqueous solutions of the cerium salts and the depolarisers used is, however, much too small to make these cells of any value. T. E.

Electrolysis of Alkali Chlorides. I. Theory of Diaphragm Electrolysis. PHILIPPE A. GUYE (*Arch. Sci. phys. nat.*, 1903, [iv], 15, 612—622).—In the electrolysis of sodium chloride solution, the current yield is a function only of the concentrations of sodium chloride and sodium hydroxide. This is deduced by considering the

migration of the ions present. Practically the current yield depends only on the concentration of the sodium hydroxide. J. MCC.

Irregularities caused by the use of Lead Anodes in Solutions of Sodium Carbonate. KARL ELES and ED. STOHR (*Zeit. Elektrochem.*, 1903, 9, 531).—In the reduction of aromatic nitrocompounds in presence of sodium acetate, a lead anode immersed in a solution of sodium carbonate contained in a porous cell is often used. Under ordinary circumstances, the lead is coated with a thin layer of peroxide, but if the sodium carbonate contains too much chloride a thick layer of a mixture of peroxide, chloride, and carbonate of lead is formed which hinders the passage of the current. When the sodium carbonate solution is too weak and contains acetate, the peroxide coating falls off and the lead is converted into carbonate. To avoid these irregularities, not less than 15 c.c. of a cold saturated solution of pure sodium carbonate should be used per ampere hour. T. E.

Valvular Action and Pulverisation of Copper Anodes. FRANZ FISCHER (*Zeit. Elektrochem.*, 1903, 9, 507—509).—An anode consisting of a wire of pure copper, 2 mm. thick, is immersed to a depth of 10 mm. in sulphuric acid of maximum conductivity, a copper plate serving as cathode. When an *E.M.F.* of 20 volts is applied, pulverisation of the anode accompanied by a singing sound takes place, a cloud of copper-coloured dust is formed, and copper sulphate is found in the solution. If a gradually increasing *E.M.F.* is used, the formation of a coating on the anode can be observed which is suddenly pulverised when the *E.M.F.* has reached about 20 volts, the pulverisation being accompanied by a sudden increase in the current to more than 50 times its initial value. A thermometer enclosed in a hollow cathode registered 106—108° at the moment of pulverisation. The author supposes that the coating which forms on the anode consists of cuprous sulphate; owing to its high resistance, it becomes heated until finally the liquid contained in its pores boils and disperses it suddenly into the surrounding cold solution, where it decomposes into cupric sulphate and finely-divided metallic copper.

By cooling the cathode internally, pulverisation occurs at a much higher voltage. The resistance of the anode coating diminishes as the temperature rises and disappears at about 80°. In more dilute sulphuric acid, or in a solution of sodium sulphate, cuprous hydroxide is formed instead of the finely-divided copper. The behaviour of aluminium in sulphuric acid is quite similar in many ways to that of copper; by cooling an aluminium anode internally, the non-conducting layer will withstand 220 volts, whilst under ordinary circumstances 20 volts suffice to break it down. T. E.

Law of the Recombination of the Ions. P. LANGEVIN (*Compt. rend.*, 1903, 137, 177—179. Compare this vol., ii, 263).—It has been experimentally proved that in electrified gases the ratio of the number of recombinations to the number of collisions between ions of opposite signs varies proportionally with the square of the pressure.

Recombination takes place when the centres of the ions, in their

motion, approach each other, so that the distance is less than a definite quantity. J. McC.

The Course of the Melting Point Line of Alloys. III. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 21—30. Compare this vol., ii, 266).—The author points out the importance of the term $\log(1-x)$ in the equation representing the melting point line. The formula $T' = T_0[(1+x)/(1+rx)^2]/1 - \log(1-x)$, which has been shown to apply to tin amalgams, is generally applicable, provided that no mixed crystals form in the solid phase. Deviations from this formula are to be attributed either to the formation of mixed crystals or to the dissociation of associated molecules. Heycock and Neville's results (*Abstr.*, 1897, ii, 245) with silver-lead and silver-tin alloys are discussed. It is proved that, at any rate for low concentrations, silver dissolved in lead exists in monatomic molecules, and this applies probably also to silver dissolved in tin.

The points of inflection of melting point curves are treated mathematically, and it is shown that the question as to whether or not a point of inflection occurs can be settled by determining whether or not the value of the latent heat of fusion is greater than four times the melting point. J. McC.

Regularities in the Composition of the Most Fusible Mixtures of Pairs of Inorganic Salts. OTTO RUFF and WILHELM PLATO (*Ber.*, 1903, 36, 2357—2368).—The paper contains the freezing point curves of 37 series of binary mixtures of inorganic salts, determined by means of a platinum | platinum-iridium thermo-couple. A number of relations between the proportion of anion in the eutectic mixture of each series and the atomic weights of the anions and cations are pointed out, for which reference must be made to the original paper. Several pairs of salts, such as KBr—KCl, NaBr—NaCl, KI—KBr, and CaCl_2 — CaBr_2 , show no distinct eutectic point, and in these cases the existence of a continuous series of mixed crystals is probable. No theoretical explanation of the regularities found is offered.

The following freezing points of inorganic salts were determined with the same pyrometer, and under identical conditions:

BaF_2	1280°	CaF_2	1330°	CdF_2	over 1000°	KF	885°	NaF	980°
BaCl_2	960	CaCl_2	780	CdCl_2	590	KCl	790	NaCl	820
BaBr_2	880	CaBr_2	760	CdBr_2	350	KBr	750	NaBr	765
BaI_2	740	CaI_2	740	CdI_2	1000	KI	705	NaI	650
						K_2SO_4	1050	Na_2SO_4	880

C. H. D.

Sublimation Curves. ALBERT BOUZAT (*Compt. rend.*, 1903, 137, 175—176).—From a comparison of the sublimation curves of carbon dioxide, ammonium hydrogen sulphide, and ammonium carbamate with the dissociation curve of the compound $\text{AgCl}\cdot 3\text{NH}_3$, it is proved that the ratio of the pressures is constant, just as has been found for the ratio of the dissociation pressures (this vol., ii, 529). The curves for: solid \rightleftharpoons solid + gas, and for solid \rightleftharpoons gas, can be deduced from each

other with the aid of the law $T_B/T_A = \text{const.}$ By applying Clapeyron's formula, it can be deduced that the variation of entropy corresponding with the passage of a molecule from the solid to the gaseous state at a definite pressure has the same value in all the systems: solid \rightleftharpoons solid + gas, and solid \rightleftharpoons gas. J. McC.

Heat of Neutralisation of Hydroferrocyanic Acid. Heat of Formation of its Compounds with Ether and with Acetone. PAUL CHRÉTIEN and JOSEPH GUINCHANT (*Compt. rend.*, 1903, 137, 65—68. Compare this vol., i, 612).—The heat of neutralisation of hydroferrocyanic acid by 4 molecules of potassium hydroxide is 57.9 Cal. at 12°. The combination of a molecule of solid hydroferrocyanic acid with ether vapour develops 11 Cal. per molecule of ether fixed. When an aqueous solution of hydroferrocyanic acid is covered with a layer of ether, colourless, octahedral crystals slowly form at the surface of separation. These crystals effloresce rapidly in the air.

The combination of solid hydroferrocyanic acid with acetone vapour develops 9.7 Cal. per molecule of acetone.

These heats of formation are nearly the same as the heats of formation of the additive compounds of ammonia with metal chlorides, and the dissociation tensions of the two classes of compounds will therefore be of the same order of magnitude according to de Forcrand's empirical rule (this vol., ii, 267). J. McC.

Laws and Equations of Chemical Equilibrium. ARIÈS (*Compt. rend.*, 1903, 137, 253—255).—By considering the potentials of a system in equilibrium, it is deduced that the potential of the same mass of any substance whatever has the same value in all the phases in which the substance may exist. Every chemical reaction takes place with the same equivalence between the molecular potentials as between the molecular weights, and the potential of a compound is equal to the sum of the potentials of the constituent atoms.

J. McC.

Various Catalytic Reactions brought about by Metals: Activating and Paralysing Influences. J. AUGUSTE TRILLAT (*Compt. rend.*, 1903, 137, 187—189).—The author refers to the various actions in which hot spirals of copper or platinum play a catalytic part.

The oxidising action is shown by the oxidation of alcohols to aldehydes. The conversion of alcohols to aldehydes in absence of oxygen shows the dehydrogenising action of these metals.

The condensation action is illustrated by passing a current of methyl alcohol and formaldehyde over a platinum spiral (*Abstr.*, 1902, ii, 602), when methylal is formed.

The incandescent spiral also exerts a saponifying action. When methylal and water vapour are passed over the spiral, formaldehyde and methyl alcohol are produced. Ethyl acetate and ethyl bromide are hydrolysed in the same way.

When moist trioxymethylene is passed over the spiral, methylal is

formed ; in this case, it is necessary to assume the intermediate formation of methyl alcohol.

The superposition of catalytic actions is demonstrated by the conversion of dimethylaniline into tetramethyldiaminodiphenylmethane, $\text{CH}_2[\text{C}_6\text{H}_4\cdot\text{NMe}_2]_2$. The formation of this implies (1) the oxidation of a methyl group, and (2) the condensation of the dimethylaniline with the formaldehyde formed.

Bright copper is not serviceable for these actions ; it should be first heated in the flame so as to become covered with a layer of oxide. The copper becomes more active as it is used. The presence of some metals in the copper aids the action, whilst that of others retards it.

J. McC.

A New Chemical Theory. LUDWIG ZESCHKO (*J. pr. Chem.*, 1903, [ii], 68, 120—129).—This is an attempt to combine the structural with the dualistic theory. The paper is not suitable for abstraction.

G. Y.

Inorganic Chemistry.

The Bromides of Sulphur. OTTO RUFF and GEORG WINTERFELD (*Ber.*, 1903, 36, 2437—2446).—Pure sulphur bromide may be prepared by heating sulphur with bromine at 100° in a sealed tube. The garnet-red product may be distilled under reduced pressure, and boils at $57\text{--}58^\circ$ under 0.22 mm., at 54° under 0.18 mm., and at 52.5° under 0.145 mm. pressure. The sp. gr. at 20° is 2.6355, and the melting point -46° ; $n_{\text{D}^{20}}$ 2.6268. The melting points of a series of mixtures of bromine and sulphur bromide were observed by a similar method to that employed by Ruff and Fischer for sulphur chloride (this vol., ii, 204). No accurate results could be obtained from mixtures containing less than 71 per cent. of bromine on account of the great supercooling, causing crystals of sulphur to separate. The curve illustrating the results from 71.38 to 93.03 per cent. of bromine consists of two branches only, meeting in a eutectic point at -59.5° , corresponding with about 80 per cent. bromine. The curve is quite regular, and shows no indication of the existence of SBr_2 or SBr_4 . The vapour pressures of mixtures of sulphur bromide and bromine were determined by Wohl's gasometric method (this vol., ii, 39). The curves of vapour pressure and of specific gravity show no change of direction between 71.38 and 100 per cent. of bromine. Attempts to prepare double compounds with other bromides were unsuccessful. There is, therefore, no evidence of the existence of the compounds SBr_2 and SBr_4 .

C. H. D.

Action of Ammonium Persulphate on Metallic Oxides. ALPHONSE SEYEWETZ and P. TRAWITZ (*Compt. rend.*, 1903, 137, 130).—From a study of the action of ammonium persulphate on metallic oxides, results differing from those with hydrogen peroxide have been obtained.

With protoxides, the ammonia may be displaced with formation of the corresponding persulphate or of sesquioxides or peroxides.

With sesquioxides or peroxides, part of the ammonia may be oxidised with evolution of nitrogen and formation of the corresponding sulphate, or the sulphate is formed and oxygen is evolved, or complete peroxidation may take place. J. McC.

Conditions of Formation and Stability of Thiosulphuric Acid. JULES ALOY (*Compt. rend.*, 1903, 137, 51—53).—When a current of sulphur dioxide is passed through a suspension of sulphur in 95 per cent. alcohol, thiosulphuric acid is formed; at 20°, about 1·8 grams per litre are formed. In alcoholic solution or in aqueous solutions of normal salts, thiosulphuric acid is comparatively stable; in pure aqueous solution, sulphur is quickly deposited. The decomposition takes place somewhat more quickly in sunlight than in the dark. The decomposition is greatly accelerated by the presence of acids, and the influence is dependent on the ionisation of the acid. The decomposition is retarded by the presence of sulphurous acid. J. McC.

Nitrites. FRITZ VOGEL (*Zeit. anorg. Chem.*, 1903, 35, 385—413).—*Barium nitrite*, prepared by Arndt's method (*Abstr.*, 1901, ii, 507) from silver nitrite and barium chloride solutions and precipitation with alcohol, has the formula $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$. It loses its water of crystallisation at temperatures above 30°; the anhydrous salt is somewhat hygroscopic. The crystals for crystallographic measurement were obtained by placing a layer of alcohol over a concentrated aqueous solution of the nitrite. The crystals belong to the hexagonal system, and show the combination $\infty P, P$, and frequently also the basal plane, OP . One hundred c.c. of water dissolve 58 grams of barium nitrite at 0°, 63 grams at 20°, and 97 grams at 35°. The solubility in mixtures of alcohol and water was determined; it is insoluble in mixtures containing more than 90 per cent. of alcohol.

Strontium nitrite, $\text{Sr}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, obtained in the same way, is stable in dry air but is hygroscopic. When heated, it loses its water of crystallisation, but more difficultly than the barium salt; the crystals, which are hexagonal, show only the combination $\infty P, OP$. One hundred c.c. of the saturated solution at 19·5° contain 62·83 grams of $\text{Sr}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, and 100 c.c. of solution in absolute alcohol contain 0·04 gram at 20°.

Calcium nitrite was prepared in the same way, but could not be so readily precipitated by alcohol. The salt was therefore obtained by evaporation of the solution; it easily loses water in the air, and is difficult to obtain exactly in the state represented by the formula $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$. At 20·5°, 100 c.c. of water dissolve 111·6 grams of $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, and 100 c.c. of alcohol at 20° dissolve 1·1 grams. The crystals resemble those of barium nitrite, but do not grow so well.

The nitrites of barium, strontium, and calcium form an isomorphous group.

The other nitrites were prepared by the action of the sulphates of the metals on barium nitrite.

Magnesium nitrite, $\text{Mg}(\text{NO}_2)_2 \cdot 3\text{H}_2\text{O}$, forms leafy crystals and is soluble in water and alcohol, but after partial dehydration over sulphuric acid it does not give a clear solution.

Lithium nitrite, $\text{LiNO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, was obtained in thin, prismatic crystals, when a layer of ether is placed over its alcoholic solution; it is extremely hygroscopic.

Thallous nitrite, TlNO_2 , was obtained as a yellow, crystalline mass. From aqueous solution, alcohol precipitates the thallous nitrite as a fine, light yellow powder. The salt is unaffected by heating at 140° . The thallium was estimated by titration with permanganate.

When beryllium, zinc, or cadmium sulphate in molecular proportion is added to a solution of barium nitrite, decomposition occurs, and it has not been possible in any case to isolate a salt containing metal and NO_2 in the proportion of 1:2.

The conductivities of barium, strontium, and calcium nitrites have been determined at 25° at various dilutions. The conductivities are about the same for the three salts and higher than those for the corresponding nitrates.

The transport number of the cation of barium nitrite was found to be 0.4123, and that of the anion 0.5877; the mobilities are $l_c = 43.29$ and $l_a = 61.71$.

Results of the depression of the freezing point of water lead to the value 2.54 for van't Hoff's factor i for 2*N*-barium nitrite solution, and 2.48 for 0.2*N*-solution. J. McC.

Preparation of Hyponitrous Acid. HEINRICH WIELAND (*Ber.*, 1903, 36, 2558—2567).—See this vol., i, 690.

Action of Phosphorus on Hydrazine. JOHANNES W. DITO (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 1—4).—When yellow phosphorus (6 atoms) and a 90 per cent. solution of hydrazine (1 mol.) are left in contact in a vacuum tube for a month or two at the ordinary temperature, a black, amorphous solid is produced, throughout which is distributed a white, crystalline substance, and when the tube is opened hydrogen phosphide escapes. The white substance, which is either hydrazine phosphite or hydrazine hypophosphite, was extracted with alcohol. The black mass is insoluble in alcohol, ether, and carbon disulphide, and in contact with air becomes moist and assumes a yellow colour. On distilling with dilute sodium hydroxide, it gives hydrazine. It is attacked by dilute nitric acid and by bromine; when heated at 100° in a current of hydrogen, it loses weight and becomes red. The red substance gives black products with alkalis, but on continued washing the original substance is regenerated; it is free from nitrogen and contains 91.7 per cent. of phosphorus and 1.1 per cent. of hydrogen, the remainder being probably oxygen. It is a weak acid, and the black substance is its hydrazine derivative.

The same red substance can be obtained when phosphorus and free hydrazine are employed. J. McC.

Reaction between Yellow Phosphorus and Copper in Aqueous Solution. WALTHER STRAUB (*Zeit. anorg. Chem.*, 1903, 35, 460—473).—When phosphorus is placed in an aqueous solution of copper sulphate, it becomes black, and when removed from the solution it does not react with the atmospheric oxygen. In the solution, the black coating becomes red on account of the deposition of metallic copper. Copper continues to be deposited as long as phosphorus is present, but in all cases the black deposit is first formed. This black substance is a copper phosphide, but its composition could not be accurately ascertained. As the reaction proceeds, the quantity of phosphoric acid in the solution continuously increases. It has been established that the quantity of phosphorus which enters into reaction only stands in a constant relationship to the amount of reduced copper sulphate if the reaction is not carried to an end or if atmospheric oxygen is rigorously excluded. At the point where the reaction is just complete, the solution contains sulphuric acid and phosphoric acid in the proportion 1:0.5, and consequently 1 mol. of phosphorus separates 2 mols. of copper from the copper sulphate solution. The oxygen which oxidises the phosphorus must come from the water because the amount of sulphuric acid undergoes no diminution. The reduced copper is not acted on by the sulphuric acid, but is oxidised by the atmospheric oxygen, and the copper oxide dissolves to form copper phosphate, which is then reduced to phosphide. The dark film on the phosphorus is produced in a solution containing only 1 gram-mol. of crystallised copper sulphate in 100,000 litres of water, and at a dilution 10 times as great the film is produced in the course of two months.

A layer of olive oil containing phosphorus was placed over water in an apparatus which permitted of the access of air only to the water, and a strip of copper was placed in the water. The aqueous layer becomes black and opaque, and when removed from the oil deposits the black phosphide. The liquid again placed in contact with the oil and with the copper strip immersed becomes black; this can be repeated until the phosphorus is completely removed from the oil. At the same time, the quantity of phosphoric acid in the solution increases, and the conclusion is drawn that the phosphide is oxidised by atmospheric oxygen to phosphate, and in contact with phosphorus the oxygen is withdrawn so that phosphide is regenerated. The copper phosphide, therefore, acts as an oxygen carrier. J. McC.

Arsenic in Sea-water, Salt Deposits, Table Salt, Mineral Waters, &c. Its Estimation in some Ordinary Reagents. ARMAND GAUTIER (*Compt. rend.*, 1903, 137, 232—237).—The method already described (this vol., ii, 612) for the estimation of arsenic has been applied to sea-water, salt deposits, table salt, mineral waters, and some reagents.

In sea-water, taken 30 metres off the coast of Brittany at a depth of 5 metres, the mineral arsenic amounted to 0.009 mg. per litre and

the organic arsenic to 0.0008 mg. per litre. In water taken from the Atlantic near the Azores, the amount of arsenic varied from 0.01 to 0.08 mg. per litre according to the depth. The large quantity of arsenic in sea-water at this place is connected with the volcanic actions which take place in the neighbourhood.

All the specimens of sodium chloride from different sources examined contained arsenic, and it was found that that intended for culinary purposes contained, as a rule, the largest quantity; the quantity is such as to be important from a medico-legal point of view, because arsenic is thus introduced normally into the system.

Several of the mineral waters from Vichy were examined and all contained arsenic; the results obtained agree well with those found by Willm.

All the reagents tested, with the exception of zinc, were found to contain arsenic. Distilled water, nitric acid, sulphurous acid, the ordinary hydrogen sulphites, ammonia, and ammonium carbonate are amongst the reagents which contain traces, and it is constantly present to an appreciable extent in hydrogen sulphide.

The author calculates that by the method described (*loc. cit.*) it is possible to estimate 0.001 to 0.0005 mg. of arsenic. J. McC.

Action of Ozone on Carbon Monoxide. C. E. WATERS (*Amer. Chem. J.*, 1903, 30, 50—53).—Since the results obtained by Jones (see preceding abstract) do not agree with those of previous observers on the action of ozone on carbon monoxide, the work was repeated, the same ozoniser being used, but the induction coil being replaced by a Holtz machine. It was found that oxidation does not take place to an appreciable extent at the ordinary temperature, but that at 240—280° some carbon dioxide is produced, the amount depending on the concentration of the ozone. E. G.

Action of Ozone, Hydrogen Peroxide, &c., on Carbon Monoxide. WM. A. JONES (*Amer. Chem. J.*, 1903, 30, 40—50).—It has been stated by Baumann (*Abstr.*, 1882, 691) and by Leeds (*Abstr.*, 1884, 15) that when a mixture of carbon monoxide and air is passed over moist phosphorus, carbon dioxide is produced. Remsen and Keiser (*Abstr.*, 1884, 149), however, found that no oxidation of the carbon monoxide took place under these conditions. In the present paper, experiments are described which show that some carbon dioxide is always formed, but that the amount varies with the quantity of phosphorus exposed and the rate at which the gas is passed over it. When pure carbon monoxide is brought into contact with phosphorus immersed in a solution of hydrogen peroxide, carbon dioxide is not produced, and it is therefore very improbable that the oxidation of carbon monoxide by air and moist phosphorus is due to the action of the phosphorus on hydrogen peroxide formed in the course of the experiment.

In view of the statement of Remsen and Southworth (*Abstr.*, 1876, i, 341) that carbon monoxide is not oxidised by ozone either at the ordinary temperature or at 300°, experiments were carried out in which the ozone, prepared by means of a Berthelot ozoniser and a

Ruhmkorff coil, was probably of a greater concentration than that used by those authors. The results show that by the action of oxygen containing 3.78 per cent. of ozone, carbon monoxide is oxidised to some extent at the ordinary temperature and to a much larger extent at 250°. The action of the ozone formed by the oxidation of moist phosphorus was also examined at 250°, and it was found that, in general, the oxidising power of ozone varies with the temperature and the concentration.

It has been stated by Remsen that carbon monoxide is not oxidised by solutions of hydrogen peroxide of the usual strength. This statement has now been confirmed, and it has been found that no oxidation occurs even when solutions containing as much as 63 per cent. of hydrogen peroxide are used.

When carbon monoxide is led into a U-tube in which acidified water is undergoing electrolysis and is allowed to bubble directly against the electrode at which the oxygen is being evolved, no carbon dioxide is produced. Electrolytic oxygen, therefore, has not the power of oxidising carbon monoxide.

E. G.

Silicates. III. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1903, 35, 336—346. Compare this vol., ii, 475, 542).—Barium silicate, $\text{BaSiO}_3 \cdot \text{H}_2\text{O}$, was boiled for 8 to 10 hours with water, and the composition of the part which had dissolved and that of the residue were determined. The residue was then boiled with water and so on until the substance had been treated ten times. Provided that there is not less than 29 grams of the silicate to one litre of water, the solubility is about 1.28 grams per litre, and the composition of the substance in solution is to be represented by the formula $\text{BaO} \cdot 2\text{SiO}_2$. As the treatment with successive quantities of water is continued, the proportion of base which passes into solution increases, and consequently the proportion of silica in the residue also increases. It is also proved that for the extraction of a given quantity of silicate with a definite amount of water it is not a matter of indifference whether the water is used in several small lots or in one large amount. In some cases, the aqueous extract on evaporation gave crystals of the formula $\text{BaO} \cdot 6\text{SiO}_2$.

Similar results were obtained with strontium and calcium silicates.

The stability of the silicates towards carbon dioxide decreases as the atomic weight of the base increases.

Dissociation and hydrolysis are not sufficient to explain the observed results; it seems probable that by the action of water the anion undergoes some change, so that the ion of a pyro-acid is formed. More experimental data are required, however, before definite conclusions may be deduced.

J. McC.

Bibliography of the Metal Alloys. M. SACK (*Zeit. anorg. Chem.*, 1903, 35, 249—328).—The author has collected the bibliography concerning alloys. It is catalogued alphabetically according to authors and indexed according to metals.

J. McC.

Double Salts of the Alkali Group. HERMANN GROSSMANN (*Ber.*, 1903, 36, 2499—2502. Compare this vol., ii, 476).—Polemical. A reply to Ephraim (this vol., ii, 538). A. McK.

Composition of Halogen Salts. PAUL PFEIFFER (*Ber.*, 1903, 36, 2519—2523. Compare Ephraim, this vol., ii, 418, 538, 552).—The double salts of MgBr_2 , ZnBr_2 , PdBr_2 , IrBr_2 , AuBr_3 , UrBr_4 , OsBr_4 , IrBr_4 , PtBr_4 , SnBr_4 , SeBr_4 , SnI_2 , IrI_3 , AsI_3 , IrI_4 , PtI_4 , TeI_4 are similarly constituted whether the associated haloid is the ammonium, lithium, sodium, potassium, rubidium, or caesium salt. Again, in certain cases, the alkali metals of highest atomic weight form double salts containing a maximum number of molecules of the alkali haloid, as in $\text{PbBr}_2 \cdot 4\text{CsBr}$; $\text{TlBr}_3 \cdot 3\text{RbBr}$; $\text{ZnI}_2 \cdot 3\text{CsI}$; $\text{CdI}_2 \cdot 3\text{CsI}$; $\text{HgI}_2 \cdot 3\text{CsI}$; whilst in other cases the ammonium salt represents the highest type, as in $\text{CdBr}_2 \cdot 4\text{NH}_4\text{Br}$; $\text{SbI}_2 \cdot 4\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$; $\text{BiI}_3 \cdot 4\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$. A similar irregularity occurs amongst the salts containing the minimum number of molecules of alkali haloid, namely, the caesium and ammonium salts of PbI_2 , the potassium salts of CuBr_2 and HgBr_2 , the sodium and potassium salts of ZnI_2 , and the ammonium salts of FeBr_3 and HgI_2 .

Similar irregularities are found on comparing the double salts formed from a given alkali metal, as in the ammonium salts AmMgBr_3 ; Am_2CuBr_4 ; Am_3ZnBr_5 ; Am_2PdBr_4 ; Am_4CdBr_6 ; Am_2SnBr_4 ; Am_2PbBr_4 ; and in the caesium salts CsMgBr_3 ; CsNiBr_3 ; Cs_3CoBr_5 ; Cs_2CuBr_4 ; Cs_3ZnBr_5 ; Cs_3CdBr_5 ; Cs_3HgBr_5 ; Cs_4PbBr_6 ; where no relationship is observed between the atomic weight of the polyvalent metal and the complexity of the salt.

An increasing molecular weight of the halogen has very little influence in decreasing the complexity of the double salt; only occasionally is the bromide less complex than the chloride, as in $\text{FeCl}_3 \cdot 3\text{CsCl} \cdot \text{H}_2\text{O}$ and $\text{FeBr}_3 \cdot 2\text{CsBr} \cdot \text{H}_2\text{O}$, although the iodide is less complex than the bromide in nearly half the cases.

Exceptions also occur to the rule that alkali metals of lower atomic weight combine with more water of crystallisation, although Werner has given it as a general rule that the hydrogen, lithium, and sodium salts never combine with less, and often combine with more, water than the potassium, rubidium, and caesium salts. T. M. L.

Silver as a Reducing Agent. WALTER S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1903, 25, 637—641).—When a solution of potassium dichromate, acidified with sulphuric acid, is boiled with excess of finely-divided silver, reduction takes place and an amount of silver is dissolved equivalent to 6 atoms to each molecule of dichromate.

Both chloric and iodic acids are capable of oxidising finely-divided silver according to the equation $6\text{Ag} + 6\text{HClO}_3 = \text{AgCl} + 5\text{AgClO}_3 + 3\text{H}_2\text{O}$. Silver is also readily dissolved by bromic acid.

It has been stated by Carey Lea (*Abstr.*, 1893, ii, 207) that finely-divided silver is dissolved to a small extent by dilute sulphuric acid. It is found, however, that this action does not take place except in the presence of oxygen, and that silver is not attacked by boiling sulphuric acid until the concentration of the latter reaches 74 per cent. E. G.

So-called Colloidal Silver. MAURICE HANRIOT (*Compt. rend.*, 1903, 137, 122—124. Compare this vol., ii, 368, 543).—Silicoargolic acid was prepared by adding silver nitrate solution to a mixture of potassium silicate and formaldehyde. The gelatinous mass was washed with potassium carbonate solution to remove the excess of silica, then dried. The brown substance has the percentage composition: H_2O , 12.82; SiO_2 , 66.93; Ag , 14.43; KOH , 3.83; Al_2O_3 , Fe_2O_3 , 1.71, and a trace of CO_2 . Dilute acids only slowly attack silicoargolic acid, but it is rapidly decomposed by a concentrated solution of potassium hydroxide. It is decomposed by heat, and evolves carbon dioxide and hydrogen. When treated with iodine, it absorbs an amount of the halogen greater than that corresponding with the silver present.

The author concludes that the colloidal silvers examined belong to different types, and that the proteid matter in collargol, the iron oxide in Lea's soluble silver, and the silica in silicoargolic acid are not impurities, but essential parts of the molecule which is destroyed by their removal.
J. McC.

Reducibility of some Metallic Oxides by Hydrogen and Carbon Monoxide. IRVING W. FAY and ALBERT F. SEEKER (*J. Amer. Chem. Soc.*, 1903, 25, 641—647).—When silver oxide is left in contact with pure dry hydrogen, reduction takes place; this action occurs even at temperatures considerably below 0° . Auric oxide, when treated with hydrogen at 0° , is more rapidly reduced than silver oxide. Mercurous oxide, yellow mercuric oxide, and red mercuric oxide are reduced by hydrogen at 80° , 50° , and 115° respectively, but are unaffected at lower temperatures.

Carbon monoxide is a more rapid and efficient reducing agent than hydrogen; silver oxide, auric oxide, mercurous oxide, and yellow mercuric oxide are reduced by it at 0° , whilst red mercuric oxide suffers reduction at 95° .

The differences in the temperatures at which the yellow and red mercuric oxides undergo reduction indicate that they are distinct substances, and confirm the variations previously recorded with regard to their behaviour towards chlorine, oxalic acid, iodic acid, and ammonia.
E. G.

Action of Iodine on the Copper Pellicles obtained by Ionoplastics. L. HOULLEVIGUE (*Compt. rend.*, 1903, 137, 47—50 Compare *ibid.*, 1902, 135, 626).—The thickness of the deposit of copper on glass can be measured, after iodising it, by the optical process devised by Fizeau.

There is a limit to the thickness of the copper deposit on which iodine vapour can completely react. The results indicate that the smallest molecule of copper capable of reacting chemically on iodine vapour has dimensions of the order of $40\ \mu\mu$, and its weight is of the order of 5×10^{-13} milligram.
J. McC.

Copper Ammonia Compounds. ALBERT BOUZAT (*Ann. Chim. Phys.*, 1903, [vii], 29, 305—383. Compare Abstr., 1902, ii, 190, 502, 550, 607; this vol., ii, 21).—A detailed account of work already published.
J. McC.

Metal-ammonia Hydroxides. W. BONDORFF (*Ber.*, 1903, 36, 2322—2326. Compare Euler, this vol., ii, 544).—Determinations of potential, conductivity, solubility, and measurements of the concentration of hydroxyl ions were made with the complex ammonia hydroxides of copper, nickel, zinc, cadmium, and silver. The potential measurements were made according to Bodländer (*Abstr.*, 1902, ii, 248). The molecular coefficient of ammonia in cadmium-ammonia hydroxide is four times that of cadmium, whence the cation has the probable structure $\text{Cd}(\text{NH}_3)_4$. Determinations of the transport numbers in the case of zinc-ammonia hydroxide show that zinc migrates to the cathode only; the cation probably has the structure $\text{Zn}(\text{NH}_3)_3$. Silver-ammonia hydroxide is more strongly electrolytically dissociated than barium hydroxide. The conductivity determinations indicated that, in order of strength, cadmium-ammonia hydroxide follows silver-ammonia hydroxide, and then come copper- and nickel-ammonia hydroxides, whilst zinc-ammonia hydroxide is a very weak base. Results from determinations of the concentration of the hydroxyl ions by the dilatometric method of Koelichen (*Abstr.*, 1900, ii, 395) corroborated those from the conductivity experiments. A. McK.

A Combination of Two Substances which takes place by Rise of Temperature and decomposes below -79° . DÉSIRÉ GERNEZ (*Compt. rend.*, 1903, 137, 255—257).—Into a tube of 2 mm. bore sealed at one end, a few crystals of red mercuric iodide were introduced and a layer of acetone about 8 cm. in depth. The tube, placed almost horizontally so as to aid dissolution, was heated to 56.4° in a water-bath. It was then held vertically until all the suspended particles settled, and after drying was immersed in liquid air. On removal from the liquid air, it was solid and had a yellow tinge, but quickly became lemon-yellow in colour. The solid then melted to a colourless liquid, then solidification began again. When the mass was brought to the temperature of -79° in a mixture of solid carbon dioxide and acetone, the solid ultimately contracted to about 1/10 of its original volume.

When the tube was held horizontally in the air after removal from the liquid air, the same transformations took place, but the solid melted to a colourless liquid which gave a flocculent deposit; this decreased in volume as the temperature rose to that of the room. The deposit was yellow mercuric iodide, which was slowly transformed into the red variety. When the experiment was carried out in a tube of only 0.2 mm. bore, the heating in the air was so quick that these several changes became confused.

The explanation offered to account for these observations is that at the temperature of liquid air the acetone solidifies and retains some of the mercuric iodide, the colour of which at low temperature is almost white. When the temperature rises to -94.9° , the acetone melts, and the mercuric iodide, instead of being deposited, enters into combination with the acetone to form a solid, yellow, molecular compound. Below -79° , this compound gradually decomposes and mercuric iodide is produced at first in the yellow form, which then

gradually reverts to the red. When the compound has been formed, it is stable at the temperature of boiling liquid air. J. McC.

The Rendering Active of Oxygen. VIII. Autoxidation of Cerous Salts and Indirect Autoxidation. CARL ENGLER [with THEOPH. GINSBERG] (*Ber.*, 1903, 36, 2642—2651).—Measurements of the amount of oxygen absorbed by cerous salts in potassium carbonate solution, either in presence or absence of arsenic acid, proved this to be in the proportion of $1\text{Ce}:10$, that is, 1 mol. of oxygen is absorbed by two cerous residues. The cerous salt in the carbonate solution tends itself to become saturated with hydroxyl groups, leaving hydrogen atoms free, which form hydrogen peroxide with the oxygen present. In the second stage of the action, the basic ceric carbonate reacts with the hydrogen peroxide to form a ceric peroxide carbonate, $\text{Ce}_2\text{O}_3(\text{CO}_3)_3$, of which the double salt with $4\text{K}_2\text{CO}_3, 12\text{H}_2\text{O}$ was obtained by Job (*Abstr.*, 1900, ii, 657).

The formation of this peroxide is thus due to a secondary reaction and affords an illustration of indirect autoxidation. E. F. A.

Action of Carbon Monoxide on Iron and its Oxides. GEORGES CHARPY (*Compt. rend.*, 1903, 137, 120—122).—The action of carbon monoxide on iron is principally one of cementation. Below about 750° , carbon is deposited on the iron, but above this temperature no free carbon is deposited and carbon dioxide is formed. At temperatures above 900° , the velocity of cementation seems to be invariable, but, as already pointed out (this vol., ii, 430), if the action is prolonged, graphite separates in the metal. If the metal is heated in a limited supply of carbon monoxide, carburisation ceases when the pressure of the carbon dioxide reaches a certain value.

When iron oxide is heated in a current of carbon monoxide, complete reduction takes place at all temperatures between 200° and 1200° , and the residual iron is more or less carburised. Above 1100° , if the experiment is carried out in a porcelain tube, a difficultly reducible ferrous silicate is formed, but the reduction can be made complete by working with a magnesium oxide crucible. J. McC.

Compound of Ferric Sulphate and Sulphuric Acid. ALBERT RECOURA (*Compt. rend.*, 1903, 137, 118—120).—When sulphuric acid (3 mols.) is added to a concentrated solution of ferric sulphate (1 mol.), the solution gradually changes from brown to colourless, and after some time a white powder is deposited. The solid is a compound of ferric sulphate with sulphuric acid, and its composition may be represented by the formula $\text{Fe}_2(\text{SO}_4)_3, \text{H}_2\text{SO}_4, 8\text{H}_2\text{O}$. By varying the proportion of sulphuric acid, the same compound is always obtained, and if double the amount already indicated be used, the substance is very quickly formed. The compound is immediately decomposed by water, in this respect behaving differently from chromosulphuric acid, which is only slowly decomposed by water. It is a true acid with a complex radicle, and gives esters (compare succeeding abstract). J. McC.

Ferrisulphuric Acid and Ethyl Ferrisulphate. ALBERT RECOURA (*Compt. rend.*, 1903, 137, 189—191. Compare preceding abstract).—*Ethyl ferrisulphate*, $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot \text{Et}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, was obtained by dissolving ferrisulphuric acid in 96 per cent. alcohol. After keeping for some months, the solution was evaporated in a dry vacuum and the ester separated as a yellow, friable solid. It is decomposed by water, and its properties are in agreement with the above formula, which proves that ferrisulphuric acid is a dibasic acid.

When ferrisulphuric acid is heated at 100° , it loses $6\text{H}_2\text{O}$, and no further loss is experienced until the temperature reaches 135° , when H_2SO_4 and $2\text{H}_2\text{O}$ are simultaneously lost. The compound with $8\text{H}_2\text{O}$ dissolves immediately in water, but that with $2\text{H}_2\text{O}$ only slowly dissolves.

Ferrisulphuric acid is formed when ferric sulphate is dissolved in hot concentrated hydrochloric acid; at the same time, ferric chloride is produced and remains dissolved. J. McC.

Carbonatopentammine Cobalt Salts. ALFRED WERNER and N. GOSLINGS (*Ber.*, 1903, 36, 2378—2382).—Carbonatotetrammine cobalt salts, $[\text{CO}_3\text{Co}(\text{NH}_3)_4]\text{X}$, described by Vortmann and Blasberg (*Abstr.*, 1890, 14), give no reaction for carbonate ions. This is now found to be also the case with carbonatopentammine salts. *Carbonatopentamminecobalt nitrate*, $[\text{CO}_3\text{Co}(\text{NH}_3)_5]\text{NO}_3 \cdot \text{H}_2\text{O}$, is prepared by mixing a solution of 100 grams of cobalt nitrate in 50 c.c. of water with a solution of 150 grams of ammonium carbonate in 150 c.c. of water and 250 c.c. of 20 per cent. ammonium hydroxide. After 12 hours, the salt separates in dark red crystals. A pure preparation is, however, only obtained by decomposition of the iodide with silver nitrate. *Carbonatopentamminecobalt bromide*, $[\text{CO}_3\text{Co}(\text{NH}_3)_5]\text{Br} \cdot \text{H}_2\text{O}$, precipitated by alcohol from a solution of the nitrate and potassium bromide, separates from water in large, red, quadratic crystals. *Carbonatopentamminecobalt iodide*, $[\text{CO}_3\text{Co}(\text{NH}_3)_5]\text{I} \cdot \text{H}_2\text{O}$, prepared in similar manner, crystallises from warm water in irregular, red tables. Other salts could not be prepared in a pure condition on account of their great solubility in water. C. H. D.

Consequences of the Theory of Nickel Steels. CHARLES E. GUILLAUME (*Compt. rend.*, 1903, 137, 44—46. Compare this vol., ii, 548).—The author has already indicated that the anomalies presented by nickel steels can be explained by the transformation of the iron from the α - to the γ -condition and *vice versa*.

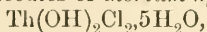
If this theory is correct, the abnormal variation of the modulus of elasticity can be explained by the passage of iron from the β - to the γ -condition.

The change of volume of nickel steels in a magnetic field is sometimes as much as fifty times as great as the change in iron. From this and Curie's results on the magnetic susceptibility of iron, it is concluded that for iron, either pure or dissolved in nickel, the condition depends not only on the temperature and on the pressure, but also on the magnetic field, and this becomes a third factor in the application of the phase rule to steels.

The anomalies exhibited by nickel steels are due to the solution of

iron in a medium which consists of a magnetic metal, the transformation temperature of which is lower than that of iron; since nickel is the only metal of this nature, it is not to be expected that these anomalies will occur in any other alloys. J. McC.

Thorium Compounds. ARTHUR ROSENHEIM, VICTOR SAMTER, and J. DAVIDSOHN (*Zeit. anorg. Chem.*, 1903, 35, 424—453).—Freshly precipitated thorium hydroxide was treated with alcohol saturated with hydrogen chloride, and on evaporating the alcohol over sulphuric acid, yielded fine, white needles of *thorium hydroxychloride*,

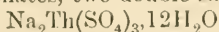


which are soluble in water. If the alcoholic solution is not saturated with thorium hydroxide, the salt which separates on evaporation and crystallises in white, shining leaflets has the formula $\text{Th}(\text{OH})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$. From the mother liquor, *thorium tetrachloride* is obtained; it has been isolated as *octohydrate*, $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$, and as *enneahydrate*, $\text{ThCl}_4 \cdot 9\text{H}_2\text{O}$, the former in prismatic needles and the latter in rhombic, transparent crystals. Both hydrates are hygroscopic, and over sulphuric acid they lose water and hydrogen chloride. Rosenheim and Schilling (*Abstr.*, 1900, ii, 351) have obtained the stable double salt, $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{ThCl}_6$; from a solution of thorium hydroxide in alcoholic hydrogen chloride by the addition of pyridine hydrochloride, the quinoline derivative is obtained in fine needles; it appears to have the formula $(\text{C}_9\text{H}_7\text{N})_2 \cdot \text{H}_2\text{ThCl}_6$, but is very unstable.

From thorium hydroxide and an alcoholic solution of hydrogen bromide, the following salts have been obtained: $\text{Th}(\text{OH})_2\text{Br}_2 \cdot 4\text{H}_2\text{O}$, easily soluble in water; $\text{Th}(\text{OH})\text{Br}_3 \cdot 10\text{H}_2\text{O}$; $\text{ThBr}_4 \cdot 10\text{H}_2\text{O}$ as acicular crystals. In the same way, with hydrogen iodide, the salts formed are: *thorium hydroxyiodide*, $\text{Th}(\text{OH})\text{I}_3 \cdot 10\text{H}_2\text{O}$, as colourless prisms which evolve iodine in the light, and thorium tetraiodide, $\text{ThI}_4 \cdot 10\text{H}_2\text{O}$, as prismatic crystals which decompose rapidly.

Thorium fluoride and its double salts with the alkali fluorides are insoluble in water and in hydrofluoric acid, and it is impossible to determine whether they are true chemical compounds or mixtures. $\text{K}_2\text{ThF}_6 \cdot 4\text{H}_2\text{O}$ is obtained from thorium hydroxide and potassium fluoride in presence of hydrofluoric acid. The flocculent precipitate obtained by treating a solution of thorium chloride with potassium hydrogen fluoride has possibly the composition $\text{KTh}_2\text{F}_9 \cdot 6\text{H}_2\text{O}$; when the precipitation is carried out with neutral potassium fluoride, $\text{KThF}_5 \cdot \text{H}_2\text{O}$ is obtained. By fusing together thorium fluoride and potassium fluoride and extracting with water, KThF_6 is obtained. When a thorium salt solution is precipitated with rubidium fluoride, $\text{RbThF}_5 \cdot 3\text{H}_2\text{O}$ is formed. These all form amorphous powders.

Potassium thorium sulphate, $\text{K}_4\text{Th}(\text{SO}_4)_4$, separates in the anhydrous form when solutions of the two salts are mixed. From mixtures of sodium and thorium sulphates, two double salts separate;



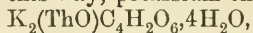
as an asbestos-like mass, and $\text{Na}_2\text{Th}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ as clear needles. Ammonium sulphate and thorium sulphate in molecular proportion give $(\text{NH}_4)_4\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, which is soluble in cold water and deposits thorium sulphate on boiling the solution. With a large excess of

ammonium sulphate, large, clear crystals of $(\text{NH}_4)_8\text{Th}(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$ are obtained. In one preparation, the salt $(\text{NH}_4)_2\text{Th}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ was produced, but the conditions for its formation could not again be found.

If sodium carbonate solution is added to a thorium salt solution until the precipitate just redissolves, alcohol precipitates a white, crystalline powder of $\text{Na}_6\text{Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$. The same double salt is produced by dissolving thorium hydroxide in a warm solution of sodium hydrogen carbonate, then precipitating with alcohol. The corresponding potassium salt, $\text{K}_6\text{Th}(\text{CO}_3)_5 \cdot 10\text{H}_2\text{O}$, is prepared in the same way. The ammonium salt has the formula $(\text{NH}_4)_2\text{Th}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, and the thallium salt is $\text{Tl}_6\text{Th}(\text{CO}_3)_5$.

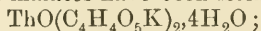
Thorium double oxalates have already been described by Brauner (Trans., 1898, 73, 951); the sodium salt, which has not before been isolated, has the formula $\text{Na}_4\text{Th}(\text{C}_2\text{O}_4)_4 \cdot 6\text{H}_2\text{O}$.

From a solution of potassium hydrogen tartrate saturated with thorium hydroxide, large, white prisms of the salt $\text{ThO}(\text{C}_4\text{H}_4\text{O}_6\text{K})_2 \cdot 8\text{H}_2\text{O}$ separate. The corresponding ammonium salt crystallises with $3\text{H}_2\text{O}$, and the sodium salt with $8\text{H}_2\text{O}$. The thorium in these compounds cannot be precipitated by alkali, so that the existence of a complex thoriotartratic molecule may be assumed. The existence of this complex is rendered very probable by the results obtained in a polarimetric examination of solutions of the salts. By the addition of a thorium salt to solutions of tartrates, the maximum rotation is observed when there is 1 mol. of thorium salt present per mol. of tartaric acid. Salts of thoriummonotartratic acid were obtained by mixing molecular proportions of a thorium salt and tartaric acid and digesting the precipitated thorium tartrate with about 8 mols. of alkali or ammonia. In this way, potassium thoriotartrate,



and ammonium thoriotartrate, $(\text{NH}_4)_2(\text{ThO})\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, were obtained. The constitution of these compounds is probably to be explained by hydrogen atoms of the alcoholic hydroxyl groups being replaced by ThO. Thorium tartrate, $\text{Th}_3\text{O}_2(\text{C}_4\text{H}_4\text{O}_6)_4 \cdot 20\text{H}_2\text{O}$, is produced as a white precipitate by mixing equivalent quantities of thorium nitrate and tartaric acid.

The following double malates have been isolated :



$\text{ThO}(\text{C}_4\text{H}_4\text{O}_5\text{Na})_2 \cdot 6\text{H}_2\text{O}$; and $\text{ThO}(\text{C}_4\text{H}_4\text{O}_5\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$. The rotatory powers of solutions of these were determined.

A series of compounds of anhydrous thorium chloride with organic compounds containing oxygen have been prepared (compare Matthews, Abstr., 1899, ii, 295, 296). The thorium chloride was prepared by Matignon and Delépine's method (Abstr., 1901, ii, 106) by passing a current of chlorine over hot thorium oxide. Thorium chloride and alcohol give prismatic, hygroscopic crystals of $\text{ThCl}_4 \cdot 4\text{EtOH}$. It does not react with ether, but with acetaldehyde it gives $\text{ThCl}_4 \cdot 2\text{CH}_3 \cdot \text{CHO}$. When suspended in ether and boiled with cinnamaldehyde, it gives long, yellow, stable needles of $\text{ThCl}_4 \cdot 2\text{CHPh} \cdot \text{CH} \cdot \text{CHO}$. Boiled with benzaldehyde, it gives an additive product, and at the same time

thorium dibenzoylchloride, $\text{Th}(\text{COPh})_2\text{Cl}_2$, in a crystalline form. With acetone, the compound $\text{ThCl}_4 \cdot 2\text{Me}_2\text{CO}$ is produced.

Thorium chloride acts on the esters of hydroxy-acids with evolution of hydrochloric acid. With methyl salicylate, it gives the compound $\text{ThCl}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, and with salicylaldehyde it reacts similarly to form $\text{ThCl}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$. A similar reaction takes place with the esters of the hydroxy-acids of the aliphatic series. Thorium chloride also reacts with 1 : 3-diketones, but the products have not yet been isolated in a pure state.

J. McC.

Double Salts of Antimony Trichloride. EDUARD JORDIS (*Ber.*, 1903, 36, 2539—2544).—A solution containing potassium and antimony chlorides was evaporated and the crystals and mother liquor were analysed from time to time. At first, much potassium chloride separated, then two successive crops of crystals had the composition $\text{SbCl}_3 \cdot 2 \cdot 3\text{KCl}$, and subsequently the proportion decreased to $\text{SbCl}_3 \cdot 0 \cdot 78\text{KCl}$. It is stated that the solid products are crystallographically uniform and not mixtures.

T. M. L.

Polonium and the Inductive Property of Radium. FRITZ GIESEL (*Ber.*, 1903, 36, 2368—2370).—The author confirms Marckwald's statement (*Abstr.*, 1902, ii, 508) that bismuth, immersed in a solution of Curie's polonium, acquires the property of emitting α -rays, but, contrary to Marckwald's observation, no trace of precipitate or coloration could be observed on the bismuth. Bismuth, platinum, and palladium may be rendered highly active by immersion in a solution of radium salt. The metal is carefully washed with hydrochloric acid and water to remove traces of radium, and then emits α -rays strongly. Bismuth becomes much more active than the other two metals, and the author's conclusion (this vol., ii, 299) is confirmed, that polonium is bismuth rendered active by contact with radium salts.

C. H. D.

Precipitation of Crystalline Gold by Formaldehyde. N. AVERKIEFF (*Zeit. anorg. Chem.*, 1903, 35, 329—335).—The ordinary reducing agents precipitate gold only in an ill-defined, crystalline state, but when gold chloride, in dilute solution, is slowly reduced by formaldehyde, the gold separates in a well-crystallised form. The precipitation is best carried out in an acid solution, and is so complete as to leave less than 0.005 gram of gold per litre in solution. The gold can be quantitatively precipitated by this method from solutions containing iron, copper, antimony, mercury, zinc, lead, manganese, tin, and arsenic.

Platinum is also precipitated from acid solution by formaldehyde, but it separates much more slowly than does gold, and on this account a perfect separation may be effected.

Gold is also reduced from solutions of the bromide, although the precipitation is not quite so complete.

The sp. gr. of the gold reduced by formaldehyde is different from that obtained by other reducing agents. At 20°, it has sp. gr. 19.43095.

J. McC.

Preparation and Properties of Ruthenium Silicide. HENRI MOISSAN and WILHELM MANCHOT (*Compt. rend.*, 1903, 137, 229—232).—*Ruthenium silicide*, RuSi , was obtained by heating a mixture of ruthenium powder and crystallised silicon in a carbon crucible in an electric furnace for two or three minutes with a current of 600 amperes at 120 volts. The product is crushed and treated with alkali, then with a mixture of hydrofluoric and nitric acids. The silicide is then left in the form of small, white crystals mixed with carborundum, from which it can be separated on account of its density by methylene iodide. If some copper be added to the mixture, the silicide is ultimately obtained in a well-crystallised form. The silicide is white, and has a metallic lustre; at 4° , it has a sp. gr. 5.40 and is very hard. It volatilises in an electric arc and is very stable. Fluorine easily attacks it, but it is only slowly attacked by chlorine. Bromine and iodine act on it slowly at 600° . When strongly heated, it burns in oxygen, and it is oxidised slowly by fused potassium chlorate or potassium dichromate. Sulphur vapour decomposes it at a red heat, and at the same temperature it is slowly attacked by fused sodium or magnesium. It is not attacked by boiling acids. Fused potassium hydroxide, carbonate, or nitrate only slowly decompose it; but when heated with a mixture of potassium hydrogen sulphate and potassium nitrate it is decomposed and a perruthenate is formed. Potassium hypochlorite, which acts easily on ruthenium, has no action on it.

For its analysis, it was decomposed by heating in a current of carbon dioxide and chlorine. J. McC.

Physiological Chemistry.

The supposed Lactic Diastase which Decomposes Salol. A. MIELE and V. WILLEM (*Compt. rend.*, 1903, 137, 135—137).—A very dilute solution of sodium hydroxide causes the decomposition of salol, and salicylic acid can be detected when any alkaline solution is in contact with salol. The decomposition of salol by milk, observed by Nobécourt and Mercklin (*Abstr.*, 1901, ii, 324), can be attributed wholly to the alkalinity of the milk or other fluids, and the authors consider that no proof has been given of the presence of a ferment which causes the decomposition. J. McC.

Employment of the Calorimetric Bomb to Demonstrate the Presence of Arsenic in the Organism. GABRIEL BERTRAND (*Compt. rend.*, 1903, 137, 266—268).—As the ordinary reagents contain traces of arsenic, this element is introduced during the destruction of organic matter under examination for arsenic. In order to avoid this, a method is adopted in which the use of many reagents is dispensed with. The author regards arsenic as a normal constituent of certain plant

and animal organs. The material is burned in a calorimetric bomb, and the liquid in the bomb is then transferred to a basin and evaporated to dryness. The residue is moistened with dilute sulphuric acid and introduced into a Marsh apparatus. By this process, no arsenic could be detected in camphor or sugar, but it was found in tortoise-shell, sponge, white and yolk of egg, &c. J. McC.

Production of Hydrogen Sulphide from the Extract of Organs and from Proteid Matter in General. J. E. ABELOUS and H. RIBAUT (*Compt. rend.*, 1903, 137, 95—96).—When sulphur is added to the extract of yeast, of animal organs, and of animal or vegetable tissues, hydrogen sulphide is formed. Roy-Pailhade supposed that this was due to the presence of a soluble hydrogenising ferment. The following observations prove that the action is not a diastasic one. When sulphur is added to an extract of horses' or calves' liver in presence of sodium fluoride and the solution made acid with tartaric acid, hydrogen sulphide is evolved at 40°. Preliminary heating of the extract even to 130° does not prevent the subsequent formation of hydrogen sulphide. If the extract is acidified and then boiled, the albumin is precipitated. The filtrate gives a small quantity of hydrogen sulphide when treated with sulphur, but the precipitate gives a much larger quantity.

Similar observations have been made with pure ovalbumin.

At 40°, no hydrogen sulphide is formed when sulphur is mixed with gelatins, peptones, or casein; but when the mixture is boiled, some hydrogen sulphide is evolved. J. McC.

Influence of Temperature on the Production of Hydrogen Sulphide by Proteid Matter, Extract of Animal Organs, and Extract of Yeast, in Presence of Sulphur. J. E. ABELOUS and H. RIBAUT (*Compt. rend.*, 1903, 137, 268—270. Compare preceding abstract).—The influence of temperature on the evolution of hydrogen sulphide when proteid matter is in contact with sulphur in a slightly acid medium has been determined. The experiments were carried out by heating a mixture of the proteid matter and sulphur at 40°, at 60—65°, at 80°, and at 95°; the hydrogen sulphide was carried by a current of an inert gas through a known volume of $N/100$ iodine solution, which was titrated after a definite time with sodium thiosulphate solution. The experiments were made with dried albumin, extract of horse liver, and extract of yeast. The quantity of hydrogen sulphide formed increases with rising temperature, and this is contrary to the assumption of hydrogenation of the sulphur by a soluble ferment. J. McC.

Toxicity of Sodium Nitroprusside. HENRI FONZES-DIACON and CARQUET (*Bull. Soc. chim.*, 1903, [iii], 29, 638—639).—Sodium nitroprusside is toxic to rabbits in doses of 0.25 gram per kilo. of body weight, whence it is probable that in doses of 17—18 grams it would be fatal to man. This toxicity may be due to the production of hydrocyanic acid, although it is probable that the salt itself exerts some action, since tetanus is produced. Hydrocyanic

acid is not formed by the action of lactic, benzoic, or dilute hydrochloric or sulphuric acids on the salt, or by the action on it of saliva, pepsin, acid-albumin, or gasterin. On the other hand, hydrocyanic acid is produced when either lactic ferment or yeast is grown in solutions containing the salt.

T. A. H.

Chemistry of Vegetable Physiology and Agriculture.

An Oxidising Bacterium and its Action on Alcohol and Glycerol. ROBERT SAZERAC (*Compt. rend.*, 1903, 137, 90—92).—When a culture medium containing glycerol is inoculated with certain wine-vinegars, cultures are obtained which have a strong reducing action on Fehling's solution. The bacteria on the culture plate are usually associated in pairs. The bacterium is easily stained by basic aniline colours. Its optimum temperature of growth is 28—30°. It does not grow on meat-broth, potato, or Pasteur's medium. It is quite different from *Mycoderma aceti* and the bacterium of sorbose. Its action on alcohol is less energetic than that of these two organisms; it only converts about 50 per cent. of the alcohol into acetic acid. Its action on polyhydric alcohols resembles that of the bacterium of sorbose. When grown on a medium containing glycerol, it oxidises this to dihydroxyacetone which is the reducing compound formed. It also oxydises erythritol and sorbitol to strongly reducing compounds, but with mannitol it does not give a reducing compound. J. McC.

Nutrition of Etiolated Plants. GUSTAVE ANDRÉ (*Compt. rend.*, 1903, 137, 199—202).—Three series of analyses of Spanish haricots, sown on June 12th, were made. In the first series, the plants were kept in darkness and taken up on July 1st; in the second, the plants were kept without light until July 1st, the cotyledons then removed, and the plants taken up on July 17th. In the third series, the plants remained in darkness until July 17th.

The results showing the relation in the composition of the plants to the seeds, and, in series 1 and 3, the relative amounts of constituents in cotyledons and plants, include determinations of dry matter, ash, nitrogen, asparagine, and soluble carbohydrates. N. H. J. M.

The Carbohydrates of Barley and their Transformations during the Course of Germination. LÉON LINDET (*Compt. rend.*, 1903, 137, 73—75).—The barley was extracted at the ordinary temperature with a solution of mercuric sulphate. The nitrogenous matter and the diastases were precipitated; the filtrate was saturated with barium hydroxide, and after filtration, sulphuric acid was added. The liquid could then be concentrated and fractionally precipitated with alcohol without any fear of the carbohydrates undergoing any

change. The precipitate obtained by the addition of barium hydroxide may contain levosin, and it was found that the quantity of this contained in barley diminishes as germination proceeds.

Alcohol at first precipitates a levorotatory gum, and after the removal of this a dextrorotatory gum separates, but no dextrin was found. The levorotatory gum is probably β -amylan; it has reducing powers, and on hydrolysis gives a mixture of dextrose and C_5 sugars. The dextrorotatory gum seems to be α -galactan; it has reducing properties, and on hydrolysis gives a mixture of galactose and levulose. These two gums are neither saccharified by diastase nor fermented by yeast; they are always present in barley: the quantity of galactan increases during germination, but that of amylan remains practically constant.

Just as the barley begins to germinate, it contains no maltose, and the absence of dextrin and maltose proves that no internal saccharification takes place during germination. The original barley contains from 0.5 to 1 per cent. of sucrose, which increases during germination to 1.5 to 3 per cent. The reducing sugar, which is probably dextrose, is present only in small quantity. As germination proceeds, the action of the sucrase becomes evident, and the quantity of dextrose and levulose increases almost proportionally with the sucrose.

The starch present diminishes by about 20 per cent. as germination proceeds.
J. McC.

Reserve Organic Matter of Chlorophyllous Plants. SWIGEL POSTERNAK (*Compt. rend.*, 1903, 137, 202—204. Compare *Rev. gén. Bot.*, 1900, 12, 5).—The greater portion (70 to 90 per cent.) of the phosphorus present in various seeds, tubers, and rhizomes was found to be present in the form of a phospho-organic acid, CH_5O_5P , which differs from phosphoric acid by the elements of formaldehyde.

The amounts of lecithin found in seeds by Töpler, Schulze, and others are relatively small, representing only 1 to 7 per cent. of the total phosphorus.
N. H. J. M.

Influence of Exterior Media in the Formation and Evolution of Odoriferous Compounds in Plants. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1903, 136, 1678—1680. Compare this vol., ii, 505).—The best results as regards the production of terpene compounds were obtained under the influence of ammonium chloride. Potassium and sodium chlorides had no appreciable effect, whilst sulphates (especially those of manganese, potassium, and ammonium), sodium nitrate, and disodium phosphate seemed to act favourably.

Increased transpiration favours etherification.

N. H. J. M.

Some Constituents of Cocoa and Kola. J. DEKKER (*Rec. trav. chim.*, 1903, 22, 143—152).—Compare this vol., ii, 619.

Chemical Constituents of Globularia Alypum. RUDOLF TIEMANN (*Arch. Pharm.*, 1903, 241, 289—306).—The results of the investigation differ from those of Schlagdenhauffen (*Abstr.*, 1883, 1025); in particular, no cinnamic acid could be detected. The leaves employed were obtained from France. They were first extracted with ether, and the extract, after evaporation of the ether, was mixed with calcined magnesia until a friable powder was obtained; this was digested with cold water, and sulphuric acid was added to the filtered liquid, when a substance was salted out in amount equal to 10 per cent. of the extract. From a solution of this in absolute alcohol, about 3.5 per cent. of a crystalline substance was obtained; this portion, *globularic acid*, $C_{26}H_{32}O_7$, melts at 228—230°, is a dibasic acid and reacts with permanganate or bromine like an unsaturated compound. The alcoholic filtrate from this acid, when mixed with water, gave a precipitate of *picroglobularin*, $C_{24}H_{30}O_7$; this is amorphous, melts and decomposes at 60—100°, has an extremely bitter taste, and is but slightly acted on by the usual reagents.

The leaves were then extracted with alcohol and the extracted matter digested with warm water; on cooling, yellow crystals separated in amount equal to 7 per cent. of the alcoholic extract, or 2.5 of the dried leaves. This substance, *globulariacitrin*, $C_{27}H_{30}O_{16}$, melts at 182—190°; when it is boiled with 1 per cent. sulphuric acid, quercetin, $C_{15}H_{10}O_7 \cdot 2H_2O$, is deposited, and the liquid is found to contain dextrose and rhamnose; these were identified by warming the liquid with phenylhydrazine acetate and crystallising the mixture of ozones fractionally from acetone. A determination of the amount of quercetin formed showed that the hydrolysis takes place in accordance with the equation $C_{27}H_{30}O_{16} + 2H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6 + C_6H_{12}O_5$. The filtrate from the glucoside-dye contains a considerable amount of choline.

C. F. B.

Constants and Composition of Myrtle Wax. WARREN RUFUS SMITH and FRANK B. WADE (*J. Amer. Chem. Soc.*, 1903, 25, 629—632).—The authors, in their investigation of myrtle wax, obtained the following results.

Sp. gr., 0.9806 at 22°/15.5°; 0.878 at 99°/15.5°; melting point, 48°; solidifying point, 45°; saponification number, 217; iodine number (Hübl), 3.9; Reichert-Meissl number, 0.5; acid number, 30.7; n_D , 1.4363 at 80°.

From these figures, it is evident that myrtle wax is mainly palmitin with some lower glyceride and a small amount of free acid. By recrystallisation from light petroleum, pure palmitin was finally obtained. No stearin could be detected.

L. DE K.

Chrysanthemums. ALEXANDRE HÉBERT and GEORGES TRUFFAUT (*Bull. Soc. chim.*, 1903, [iii], 29, 619—623).—The results of manurial experiments with chrysanthemums showed that phosphoric acid is of especial importance. The application of manures is only without effect when the soil contains at least 0.25 per cent. of total nitrogen, 0.15 per cent. of phosphoric acid, and 0.125 per cent. of potash. Comparing the produce obtained from unmanured soil with that of soil which had

complete manure, it was found that whilst the total yield was considerably increased, the percentage amounts of nitrogen and of the ash constituents were not materially altered. N. H. J. M.

Chemical Constituents of Para Cress (*Spilanthus Oleracea*). EMIL GERBER (*Arch. Pharm.*, 1903, 241, 270—289).—The plant is indigenous to Brazil. By percolation with ether, 3.2 per cent. of extract was obtained from the dry plant. Prolonged distillation of this with steam yielded an essential oil, in amount varying from 0.1 to 0.2 per cent. of the dry plant; by starting with the fresh plant, a rather better yield can be obtained. The oil was purified by treatment with hot potassium permanganate solution and fractionation under diminished pressure; the main product was *spilanthene*, $C_{15}H_{30}$, which boils at 135—138° under 25 mm., at 220—225° under atmospheric pressure, and unites with bromine in chloroform solution forming an oily *dibromide*. An acid melting at 180° was also obtained in small quantity as a product of the oxidation with permanganate.

The residue of the extract, not volatile with steam, was freed from chlorophyll by digestion with animal charcoal in ethereal-alcoholic solution and digested with 60 per cent. alcohol, which left most of the phytosterol undissolved. The alcoholic extract was evaporated, the residue digested with 10 per cent. alcoholic potash, the solution diluted with much water, boiled to expel the alcohol, and extracted with ether. The residue, after distillation of the ether, should give no crystals of phytosterol when absolute alcohol is poured over it and it is allowed to remain in a desiccator. The reddish-yellow oil, *spilanthol*, so obtained is the substance to which the characteristic taste of the cress is due; it has approximately the empirical composition $C_{37}H_{64}O_3N_2$, gives no coloration with ferric chloride, does not react like a base, contains no methoxyl, and is optically inactive. When it is treated with alcoholic potash, or, better, heated for 24 hours at 150° with dilute alcohol saturated with hydrogen chloride, the product is a monacid base, $C_4H_{11}N$, which is not identical with any of the known isomerides having this formula (neither is it piperidine; Buchheim, this Journ., 1877, ii, 196); its *hydrochloride*, *platinichloride*, and *aurichloride* melt at 163°, 232—235°, and 154—156° respectively. The other product is an *acid*, perhaps $C_{14}H_{28}O_2$.

The *phytosterol* melted at 132—133°. On one occasion, a *substance* was obtained which melted at 175—178°, but yet had the properties of a cholesterol; its empirical composition was $C_{26}H_{44}O$, and it was optically active, having $[\alpha]_D + 1.6$ in 1.5 per cent. chloroform solution.

The *fat* of the plant consists chiefly of esters of cerotic acid.

By extracting the plant with alcohol, after the extraction with ether, choline was obtained.

A considerable amount of potassium nitrate is also present.

C. F. B.

Relation of Carbon Dioxide to Proteolysis in the Ripening of Cheddar Cheese. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Amer. Chem. J.*, 1903, 30, 1—24. Compare Abstr., 1903, i, 215; ii, 388, 399).—In order to ascertain the extent to which carbon dioxide

is formed in American cheddar cheese during the process of ripening and to study the nature of the changes that give rise to the production of the gas, two cheeses were prepared, one of which was quite normal, whilst the other was made from milk containing chloroform and was kept under aseptic conditions. The experiments were carried on for 32 weeks, and the proteolytic products were then investigated.

In the normal cheese, carbon dioxide was evolved continuously, but after about 20 weeks the quantity gradually decreased; the total amount produced was equal to 0.5 per cent. of the fresh cheese. In the case of the chloroformed cheese, carbon dioxide ceased to be evolved after three weeks, and the total quantity produced only amounted to about 0.007 per cent. of the weight of the cheese.

The final products of proteolysis in the normal cheese were tyrosine, hydroxyphenylethylamine, histidine, lysine, guanidine, ammonia, and traces of arginine and putrescine. In the chloroformed cheese, the same compounds were found with the exception of hydroxyphenylethylamine, guanidine, putrescine, and ammonia; arginine, however, was present in considerable quantity.

A consideration of the possible sources of the carbon dioxide indicated that in the case of the chloroformed cheese the carbon dioxide came from that originally present in the milk and that formed in the milk by the decomposition of lactose before treatment with chloroform. In the case of the normal cheese, the earlier portions of the carbon dioxide were produced by the fermentation of lactose by lactic acid organisms, whilst a small amount was probably due to the carbon dioxide originally present in the milk and to the respiration of living organisms in the cheese; the carbon dioxide evolved after the first few weeks was apparently produced by decomposition of some of the amino-compounds.

The only active proteolytic agents in the chloroformed cheese were lactic acid ferment, galactase, and rennet-pepsin. In the experiment described, these agents were unable to form either ammonia or secondary amino-compounds with evolution of carbon dioxide; this lack of action cannot be accounted for by the presence of chloroform. It appears, therefore, that the enzymes, galactase and rennet-pepsin, are able to furnish such products as arginine, lysine, and tyrosine under the conditions existing in cheese, but are not able to convert these compounds into simpler ones with formation of carbon dioxide; hence it is probable that the latter decomposition is due to biological agency. E. G.

Analytical Chemistry.

Estimation of Aqueous Solutions with the Zeiss Immersion Refractometer. H. MATTHES and B. WAGNER (*Arch. Pharm.*, 1903, 241, 241—258).—The apparatus is now supplied with the prism pro-

jecting from the end, so that it can be used with almost any liquid. As a rule, the liquids are placed in small beakers standing in warm water, the instrument being used in a vertical position; ten of these beakers can be placed in the bath supplied, which is provided with a window in the bottom and a mirror underneath. If the liquid is very volatile, some of it is placed in a cap which slides over the prism; the end of the instrument is then immersed obliquely in water in another bath, which is supplied with a window in one side and a mirror in front of this. A second prism with matt refracting surface is also supplied, to be fixed against the first with a little of the liquid between them, as in the old Zeiss refractometer; the instrument can then be used when only a few drops of liquid can be spared. The range is from 1.32539 to 1.36640 for n_D , and the maximum error in reading the graduations is 0.00004. Calibration tables have been prepared very carefully, aqueous solutions of the chlorides, bromides, and iodides of sodium and potassium, of sodium and potassium chlorides mixed, of hydrochloric, sulphuric, phosphoric, nitric, and acetic acids, and of formaldehyde, sucrose, dextrose, alcohol, and beer extract being employed; these tables are supplied with the instrument. With their aid, the strength of new solutions was estimated and compared with what other trustworthy methods showed it to be; usually the difference was only about 0.1 per cent. of the whole, rarely more than 0.5 per cent. The instrument may be used to check the strength of standard solutions. The temperature of 17.5° was used in the calibration, and must be employed in estimations when the calibration tables are used; careful regulation of the temperature is necessary, as the variation of n_D with temperature is considerable and follows no simple law.

C. F. B.

Determination of the Neutralisation Point by Conductivity Measurement. FRIEDRICH W. KÜSTER and MAX GRÜTERS (*Zeit. anorg. Chem.*, 1903, 35, 454—459).—In using indicators in acidimetry, the colour or change of colour is only produced when the solution is either *acid* or *alkaline*. The exact point of neutralisation can be determined by conductivity measurements, because at this point a minimum conductivity is reached. The point found experimentally by conductivity lies between the points of neutralisation as indicated by methyl-orange and phenolphthalein. Incidentally, it is pointed out that solutions which have been standardised with phenolphthalein should not be used with methyl-orange, and the deviations in the results are dependent on the concentration and the presence of salts. When phenolphthalein is used as indicator, only barium hydroxide should be employed for titration.

J. McC.

Estimation of Sulphur in Urine by means of Sodium Peroxide. G. MODRAKOWSKI (*Zeit. physiol. Chem.*, 1903, 38, 562—565).—A modification of the Hoehnel-Asboth process. The author has found that the use of sodium hydroxide or carbonate and of bromine may be dispensed with. The details are as follows: 50 c.c. of urine are slowly introduced into a nickel dish containing 1 to 2 grams of sodium peroxide. After evaporating on the water-bath to a

syrupe consistence, another 2 to 3 grams of the peroxide are added little by little with constant stirring. The mass is now very gradually heated with a spirit lamp until in a state of fusion; if necessary, another 1 to 3 grams of peroxide are added. The fused mass is then dissolved in water, the filtrate is acidified with hydrochloric acid, and the sulphate precipitated as usual with barium chloride. L. DE K.

Use of Magnesia Usta in the Estimation of Amidonitrogen. FRITZ MÜLLER (*Zeit. physiol. Chem.*, 1903, 38, 286—288).—Even freshly-ignited magnesia contains small amounts of carbonate (compare Marchand and Scherer, *J. pr. Chem.*, 1850, 50, 385). When the magnesia is boiled with water, carbon dioxide is evolved, and is absorbed by the acid used for collecting the ammonia, and errors are thus introduced into the ammonia estimations. J. J. S.

New Method of Estimating Small Traces of Arsenic. ARMAND GAUTIER (*Compt. rend.*, 1903, 137, 158—163).—The method previously used by the author for estimating small quantities of arsenic requires much care, and is not available when certain other substances are present. The new method depends on the fact that when ferric hydroxide is precipitated from a solution containing arsenic, the arsenic is carried down along with the hydroxide. The iron solution to be used is prepared by dissolving ferrous sulphate in dilute sulphuric acid and oxidising with nitric acid; the ferric hydroxide is precipitated with ammonia, then filtered, and washed. The precipitate is dissolved in dilute sulphuric acid and the solution heated under reduced pressure with granulated zinc, by which process the arsenic is completely removed. The ferrous salt is oxidised by nitric acid and ferric hydroxide precipitated with ammonia; the washed precipitate is dissolved in dilute sulphuric acid, so that the solution contains 30 grams of ferric oxide per litre. One hundred c.c. of this solution contain only $\frac{1}{2}$ -thousandth of a milligram of arsenic.

To the solution to be examined for arsenic, about 5 c.c. of this ferric sulphate solution are added, and the ferric hydroxide precipitated with ammonia. The precipitate is examined by the Marsh method. Details of the process to be adopted in the estimation of arsenic in animal or vegetable matter will be given later. J. McC.

Delicacy of Tests for Arsenic in Organic Matter. ARMAND GAUTIER (*Bull. Soc. chim.*, 1903, [iii], 29, 639—643).—The author asserts, in reply to various criticisms (compare Tarugi, this vol., ii, 240), that the method of destroying organic matter recommended by him (*Abstr.*, 1876, i, 110) enables the whole of the arsenic to be obtained, and in support of this contention a series of experimental results is recorded. T. A. H.

Simplification of the Analysis of Silicates by the Use of Formic Acid. A. LECLÈRE (*Compt. rend.*, 1903, 137, 50—51).—The silicate is fused in the ordinary way with alkali, then the product is boiled with water, and formic acid is added in such quantity that the liquid

contains finally about 5 per cent. of free acid. The liquid is kept at 100° for 2 days, when the silica and titanio acid are precipitated in a form in which they can be easily filtered. The aluminium and iron are then precipitated by the addition of excess of ammonia. The formate present does not in any way prevent the precipitation of the iron or aluminium.

J. McC.

Employment of a Rotating Cathode in the Electrolytic Estimation of Metals. FRANK A. GOOCH and H. E. MEDWAY (*Zeit. anorg. Chem.*, 1903, 35, 414—419).—In order to avoid the irregularities due to the evolution of hydrogen in the electrolytic deposition of metals, the use of a rotating cathode has been tried and found to be satisfactory. As cathode, a platinum crucible is used, and it is fixed to the vertical spindle of a motor. The solution to be electrolysed is contained in a glass vessel resting on a rising table. A strip of platinum is used as anode. At first, the cathode is immersed in the solution to only about two-thirds of its depth, and it is rotated (600—800 revolutions per minute) until most of the metal is deposited. Water is then added, so that the whole crucible becomes immersed, and the electrolysis is carried to completion. The deposit is washed and dried in the ordinary way.

Results are given showing that the method is satisfactory for the deposition of copper (from copper sulphate solution containing free sulphuric acid or even nitric acid), silver (from potassium cyanide solution), and nickel (from an ammoniacal solution). As a comparatively high current strength may be used, the electrolysis can be carried out much more quickly than by the ordinary process.

J. McC.

Electrolytic Estimation of Small Quantities of Silver in Presence of Lead. GEORGES ARTH and NICOLAS (*Bull. Soc. chim.*, 1903, [iii], 29, 633—636).—A solution of the nitrates of the two metals, containing 1 per cent. of free nitric acid and a small quantity of alcohol, is electrolysed, using a current not exceeding 1.1 volt. The cathode is a cylindrical coil of platinum gauze, as recommended by Winckler, and the anode a helix of thick platinum wire. The operation is conducted at 55 — 60° and lasts for $6\frac{1}{2}$ to 8 hours. The results recorded show that as little as 0.0054 gram of silver may be estimated in presence of 100 grams of lead. The presence of copper or bismuth does not interfere with the accuracy of the method.

T. A. H.

Simultaneous Separation and Estimation of Barium, Strontium, and Calcium. LUCIEN ROBIN (*Compt. rend.*, 1903, 137, 258—259).—The metals should be present as chlorides or nitrates. If the liquid is acid, it is made slightly ammoniacal, and ammonium chloride is added. The solution is made slightly acid with acetic acid and boiled; then to the hot solution, potassium dichromate is added until the liquid has a decided yellow colour. The mixture is boiled for 5 minutes, then cooled, and filtered through a tared paper. The precipitate is washed with a 0.5 per cent. solution of ammonium acetate to which some ammonia has been added; it is then washed with 10

per cent. alcohol, dried, and weighed. A 3 to 4 per cent. solution of ammonium sulphate is added to the filtrate, and the mixture is boiled for 15 minutes, care being taken by adding ammonia that the liquid remains alkaline. The strontium sulphate is filtered off and washed with a hot 1 per cent. solution of ammonium sulphate, then with 10 per cent. alcohol; it is then dried, ignited, and weighed. The filtrate is heated to 80° , and ammonium oxalate is added. The calcium oxalate is treated in the ordinary way.

Results are given showing that when this method is followed accurate results are obtained. J. McC.

Electrolysis of Alkaline Zinc Solutions. RICHARD AMBERG (*Ber.*, 1903, 36, 2489—2494).—Whilst the quantitative electrolytic precipitation of zinc from feebly acid solutions requires constant attention during the process, this is not the case when alkaline solutions are used. For every 0.5 gram of zinc, 40 grams of potassium hydroxide are taken, and the volume of solution is made up to 150 c.c. The temperature is kept at 60 — 70° , and a current of 0.5 ampere and 3.0—3.1 volts are used. The precipitation of zinc from alkaline solutions is possible without the addition of other electrolytes. The anode was of platinum, whilst nickel was found to be very convenient for the cathode. In order to test the influence of various anions, sulphuric acid, hydrochloric acid, nitrates, tartaric acid, and potassium cyanide were each tried. Experiments on the influence of various cations are also quoted. A. McK.

Electrolytic Estimation of Thallium as Oxide by Anodic Precipitation. M. E. HEIBERG (*Zeit. anorg. Chem.*, 1903, 35, 347—354).—About half a gram of thallium sulphate is dissolved in 80 to 100 c.c. of water and the solution is placed in a matt platinum basin. Two to 6 c.c. of normal sulphuric acid solution and 5 to 10 c.c. of acetone are added, and the electrolysis carried out at 50 — 55° . The basin is made the anode and a platinum plate is used as cathode. The tension may vary between 1.7 and 2.3 volts, and towards the end may rise even to 2.5 volts. In order to prevent the deposition of thallium at the cathode, and to avoid the formation of hydroxide, the solution must be acid, but too much sulphuric acid must not be present, as the precipitated oxide is somewhat soluble in this acid. The oxide is deposited on the basin in a form which adheres well; it can be dried by means of filter paper, and subsequently for 20 minutes in an oven at 160 — 165° . J. McC.

Analysis of Bronzes and Bearing Metals. H. E. WALTERS and O. I. AFFELDER (*J. Amer. Chem. Soc.*, 1903, 25, 632—636).—*Analysis of Bronzes.*—One gram of the metal is oxidised with 10 c.c. of nitric acid, and the tin oxide is collected and weighed as usual. The filtrate is mixed with 25 c.c. of ammonia and oxidised by boiling with 5 grams of ammonium persulphate. On acidifying the solution with sulphuric acid, the lead will be left undissolved as peroxide, which is then treated with about 600 c.c. of water, 3 grams of potassium iodide, and 10 c.c. of hydrochloric acid (1 : 1); the liberated iodine is

then titrated with $N/20$ sodium thiosulphate, 1 c.c. of which represents 0.5175 per cent. of lead. The filtrate from the lead peroxide contains the copper, which may then be separated as usual by means of sodium thiosulphate and finally weighed as oxide. The filtrate from the copper contains further metallic impurities, which are estimated by the usual methods. Should manganese be present in weighable quantities, the lead should be separated by the usual sulphate method, as the peroxide would also contain the manganese.

To estimate any phosphorus, 1 gram of the sample is oxidised with nitric acid, the residue is dissolved in hydrochloric acid, and the tin, copper, and lead are precipitated with metallic zinc. The filtrate is mixed with a little ferric chloride and 10 c.c. of nitric acid, boiled, and precipitated with ammonia. The phosphoric acid contained in the iron precipitate is then determined as usual with molybdate solution.

Bearing Metals.—Tin and antimony are separated as usual as oxides. If the antimony is likely to be excessive, 0.25 gram of pure tin should be added so as to insure complete separation of the antimony. The filtrate is rendered strongly alkaline with potassium hydroxide (instead of ammonia), and the lead is precipitated by boiling with ammonium persulphate as already directed.

To estimate the antimony, 1 gram of the sample is boiled with 1 gram of potassium iodide and 80 c.c. of hydrochloric acid of sp. gr. 1.10 for 1 hour. The undissolved metallic antimony is collected on a weighed filter, washed first with boiling water and then with alcohol, dried at 100° , and weighed. It is then calculated to antimony dioxide and deducted from the weight of the joint oxides of tin and antimony.

L. DE K.

Method of Estimating Mercury Gravimetrically and Volumetrically. FRANZ M. LITERSCHIED (*Arch. Pharm.*, 1903, 241, 306—313).—When excess of potassium dichromate and then a slight excess of ammonia are added in the cold to a solution of mercuric chloride, a lemon-yellow precipitate of dimercuriammonium chromate, $(\text{NH}_4)_2\text{CrO}_4 \cdot 2\text{Hg}_2\text{O}$, is formed. This is soluble while still moist in cold 10 per cent. hydrochloric acid, when dry, in hot 25 per cent. acid; it is insoluble in ammonia provided that ammonium salts are not present in large amount; it decomposes explosively when heated.

After $\frac{1}{2}$ to 6 hours, the precipitate may be collected, dried at 100° (at which temperature none of the water is lost), and weighed. In four experiments, the error lay between -0.3 and -0.6 per cent. of the total amount.

Or the dichromate may be added in the form of a decinormal solution, 1 c.c. of which = 0.0267 gram Hg. The mixture is made up to a known volume, shaken well, left for not less than 6 hours, and filtered. An aliquot part of the filtrate is acidified with sulphuric acid and mixed with potassium iodide solution, after which the iodine liberated is titrated with $N/10$ thiosulphate. In three experiments, the error lay between -0.25 and -1.4 per cent. of the total amount.

C. F. B.

Application of Zinc for Reduction in the Estimation of Vanadic Acid. FRANK A. GOOCH and R. D. GILBERT (*Zeit. anorg. Chem.*, 1903, **35**, 420—423. Compare Abstr., 1902, ii, 700).—A glass tube, narrowed near one end, of 2 cm. bore and 50 cm. long, is sealed on to a stopcock to which is also fixed a glass tube 24 cm. long, of 0.5 cm. bore. A piece of platinum gauze is placed at the narrow point of the wide tube and it supports a layer of glass-wool 2 cm. thick, upon which rests a column about 40 cm. long, of small pieces of amalgamated zinc. The narrow tube is fitted into a filter-bottle connected with a regulator. The pressure in the bottle is reduced to about 20 cm. of water, and hot water is poured on to the zinc to warm it. About 100 c.c. of 1 per cent. sulphuric acid is poured over the zinc, then a small quantity of the vanadic acid solution to be reduced. Dilute sulphuric acid and the vanadic acid solution in small quantities are alternately poured over the zinc, which is finally washed with water. During the whole operation, the zinc must be kept covered with liquid. The filter-bottle contains a concentrated solution of silver sulphate, and this oxidises the reduced vanadium compound to vanadium tetroxide, which is titrated with permanganate. For small quantities of vanadium, the method is satisfactory, but with larger amounts the end-point of the titration is less definite. J. McC.

Quantitative Analysis by Electrolysis. XIII. Electrolytic Estimation of Antimony and its Separation from Tin. ARTHUR FISCHER (*Ber.*, 1903, **36**, 2348—2356).—The author has independently employed the method of deposition of antimony from a solution containing sodium sulphide and potassium cyanide recommended by Hollard (this vol., ii, 455). The cyanide decomposes the polysulphide formed according to the equation $\text{Na}_2\text{S}_4 + 3\text{KCN} = \text{Na}_2\text{S} + 3\text{KCNS}$. The platinum anode is slightly attacked, but no platinum is deposited on the cathode. Eighty c.c. of a sodium sulphide solution of sp. gr. 1.14 is electrolysed with a current of 0.45—0.8 ampere and a potential difference of 1.7—1.8 volt at 20—30°, 20—30 c.c. of a 30 per cent. potassium cyanide solution being added gradually. The cathode is a matt platinum basin. The separation of antimony from tin is similarly conducted, the temperature not being allowed to rise above 30°, with a potential difference of not more than 1.1 volt. The separation is complete whether trivalent or quinquivalent antimony be used. The employment of normal sodium sulphide is essential, as sodium hydrogen sulphide causes precipitation of a part of the tin unless the current-density be extremely low and the time taken very long, a small quantity of pure sodium hydroxide is therefore added to prevent the formation of sodium hydrogen sulphide. C. H. D.

Improved Seliwanoff Test. HEINRICH ROSIN (*Zeit. physiol. Chem.*, 1903, **38**, 555—556).—The liquid to be tested for keto-sugars is boiled with an equal volume of hydrochloric acid and a few particles of resorcinol. The red liquid is cooled and then rendered alkaline with sodium carbonate. On shaking with amyl alcohol, a red colouring matter is extracted which has a tinge of yellow, shows a faint green.

fluorescence, and turns red on adding a few drops of absolute alcohol. This colouring matter yields a very characteristic spectrum even after considerable dilution. Weak solutions exhibit a single absorption band in the green extending from *E* to *b*; somewhat stronger solutions give very dark and sharply-defined bands extending beyond *E* and *b*, and also another faint and ill-defined band in the blue near *F*. Concentrated solutions show general absorption from the green.

L. DE K.

New Stability Test for Nitrocellulose Powders. ALBERT P. SY (*J. Amer. Chem. Soc.*, 1903, 25, 549—570).—The powder is heated for several days, for 8 hours daily, in a specially constructed bath, which is kept at a temperature of 115° by means of a boiling mixture of xylene and toluene. Every day, the loss in weight is recorded.

The total loss of a good powder for six days is less than 10 per cent.; bad powders lose considerably more. When the heating is very prolonged, good and bad powders finally give about the same total loss.

L. DE K.

Volumetric Estimation of Alkali Nitroprussides and of Soluble Cadmium Salts. HENRI FONZES-DIACON and CARQUET (*Bull. Soc. chim.*, 1903, [iii], 29, 636—638).—Excess of an aqueous solution of cadmium nitrate of known strength is added to a known volume of the nitroprusside solution. The excess of the cadmium nitrate is determined volumetrically by titration with a standard sodium sulphide solution, using sodium nitroprusside as indicator, or the precipitated cadmium nitroprusside is dissolved in dilute ammonia solution and titrated with sodium sulphide. In either case, a violet coloration indicates the end of the reaction. The method is not applicable in presence of cyanides, ferrocyanides, or ferricyanides; the first of these may be removed by passing carbon dioxide through the boiling aqueous solution and the two latter by precipitation with zinc sulphate.

T. A. H.

Estimation of Purine Derivatives in Animal Organs by Aid of the Method of Corrected Values. RICHARD BURIAN and J. WALKER HALL (*Zeit. physiol. Chem.*, 1903, 38, 336—395. Compare His and Hafen, *Abstr.*, 1900, ii, 769; Burian and Schur, *Zeit. physiol. Chem.*, 1897, 23, 53; *Abstr.*, 1900, ii, 489; Loewi, *Arch. Exp. Path. Pharm.*, 45, 159 and 174).—Full details of Burian and Schur's method of corrected value are given, and a number of experiments have been conducted in order to test its accuracy. The conclusions arrived at are: 1. The chief precipitate contains, at most, only the merest trace of albumoses when the directions given are carefully followed. 2. The chief precipitates obtained from pancreas extracts consist of pure silver derivatives of purine bases, and, if the operation is rapidly performed, of guanine silver oxide. 3. The precipitates obtained from muscle and thymus extracts contain an impurity. This is, however, free from, or contains only traces of, nitrogen. It may be removed by precipitation with phosphotungstic acid when it

remains in the filtrate. 4. In the precipitation of the purine silver derivatives, that is, in the presence of an excess of silver, concentrated ammonia is an advantage, as it prevents the precipitation of impurities. If excess of silver is not present, then concentrated ammonia gradually decomposes the silver purine derivatives. Guanine silver oxide is decomposed into guanine and silver oxide, and hypoxanthine silver oxide is partially dissolved as such. 5. Purine bases are not completely precipitated by the addition of phosphotungstic acid to a warm solution of the bases in normal sulphuric acid, some 3.5–5.5 per cent. remaining in solution. 6. Amino-purines appear to gradually undergo conversion in animal extracts into oxypurines.

Control experiments made by adding known quantities of purine bases to extracts of different animal organs and estimating by the Burian-Schur method gave very satisfactory results.

The following numbers indicate the total purine nitrogen in 100 parts of the moist material: horseflesh, 0.055; mutton, 0.062; veal, 0.071; thymus from calf, 0.482–0.429; pig's pancreas, 0.123; and sheep's pancreas, 0.183.

The Burian-Schur method cannot be employed for the estimation of purine bases in the liquid obtained by boiling blood with dilute sulphuric acid on account of the large amounts of albumoses and the small amounts of purine bases present.

J. J. S.

Detection of Quinine in Organic Secretions, &c., by means of its Fluorescing Properties. GEORGES DENIGÈS (*J. Pharm. Chim.*, 1903, [vi], 17, 505–508).—Whilst the characteristic fluorescence shown by acid quinine sulphate does not show with ordinary artificial light, it may be observed by making use of magnesium light.

The substances freed from albumin, &c., are rendered alkaline with ammonia and agitated with ether. The ethereal layer is removed with a pipette, filtered, and agitated with dilute sulphuric acid, which will dissolve the quinine and exhibit the reaction. Very small quantities of the alkaloid may thus be detected in urine, saliva, bile, blood, milk, viscera, and pharmaceutical preparations.

L. DE K.

Tests for Strychnine; Wenzell's Reagent. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1903, [vi], 17, 553).—Wenzell's reagent (a solution of 1 part of potassium permanganate in 200 parts of sulphuric acid), although a very delicate test for strychnine, must nevertheless be used with caution as it also gives a similar, but less intense and less persistent reaction with tartrates, citrates, and thiocyanates. On the other hand, traces of foreign alkaloids may weaken or altogether prevent the reaction.

These substances are without action on a solution of ammonium vanadate or ceric oxide in sulphuric acid, but they give a green coloration when potassium dichromate is used.

L. DE K.

Estimation of Strychnine. F. J. SMITH (*Amer. J. Pharm.*, 1903, 75, 253—257).—The following modification of Keller's method gave good results in assays of liquid and solid extracts of *nux vomica*. The mixed alkaloids from 8 or 10 grams of the drug are dissolved in 15 c.c. of 3 per cent. sulphuric acid, the solution being aided by gently heating. After cooling, 3 c.c. of a cold mixture of equal parts of nitric acid of sp. gr. 1.42 and water are added. The solution is shaken occasionally for 10 minutes, then transferred to a separating funnel containing 25 c.c. of 10 per cent. sodium hydroxide solution, and extracted 3 times with chloroform. The united extracts are filtered and evaporated after adding 2 to 3 c.c. of pure amyl alcohol to prevent decrepitation of the strychnine on removing the last traces of chloroform by heating. The residue is dried for 2 hours at a temperature of 135° to 140° and weighed.

W. P. S.

Some Constituents of Cocoa and Kola and their Estimation. J. DEKKER (*Rec. trav. chim.*, 1903, 22, 143—152. Compare this vol., ii, 172).—Cocoa husks on analysis gave albumin, 10.2; fat, 3.9; theobromine, 0.5; pentosans, 9.4; water, 15.0; ash, 7.8 per cent. After subjecting the present methods of determining the xanthine bases in cocoa to a critical examination, the following new process is recommended: 10 grams of the powdered cocoa are heated with 5 grams of magnesium oxide and 300 c.c. of water in a reflux apparatus for 1 hour, and after filtering and draining on the pump the residue is again boiled with water for a quarter of an hour and again drained; the solution thus obtained is evaporated to dryness, triturated with sand, and the fine powder boiled with 100 c.c. of chloroform, the chloroform evaporated, and the residue weighed. This gives the total quantity of alkaloids present (caffeine and theobromine), and the amount of caffeine is estimated by extracting the weighed residue with 50 c.c. of cold benzene during 24 hours, evaporating 25 c.c. of the solution, and weighing the residue; under these conditions, only traces of theobromine dissolve. With this method, a cocoa which had given results with other methods ranging from 0.71—2.78 for the total alkaloids gave constant values of 1.69—1.73 per cent.; kola nuts were found similarly to contain 1.62—1.68 per cent. of alkaloid.

Young leaves of the cocoa plant contain 0.54—0.55 per cent. of theobromine, but in older leaves the proportion is much less (0.29—0.0 per cent.). In young leaves of kola, there were present 0.049 per cent. of caffeine and 0.101 per cent. of theobromine; this is remarkable inasmuch as in the kola seed the proportion of theobromine is very much less than that of caffeine.

W. A. D.

Estimation of the Products of Putrefaction in Urine and Fæces by means of Ehrlich's Aldehyde Reaction. R. BAUMSTARK (*Chem. Centr.*, 1903, i, 1444; from *Münch. med. Wochschr.*, 40, 17).—Urinary indican is determined colorimetrically by Strauss' method, the combined sulphuric acid by the process of Baumann and Salkowski, and the indole in fæces by means of dimethylaminobenzaldehyde. The ratio of indole to indican and alkyl hydrogen sulphates varies considerably.

L. DE K.

Estimation of Indican in Urine. ALEXANDER ELLINGER (*Zeit. physiol. Chem.*, 1903, 38, 178—196. Compare Wang, *Abstr.*, 1898, ii, 659, and Obermayer, 1899, ii, 263).—The method adopted is similar to that described by Obermayer, except that the indigotin should be extracted with chloroform immediately after the addition of the oxidising agent. It is also necessary to wash the residue from the chloroform solution with hot water to remove small amounts of isatin which are usually formed. The residue is then dissolved in sulphuric acid and the indigotin titrated with dilute permanganate (3 grams per litre). The numbers obtained are always low (some 84—87 per cent. of the theoretical) owing to the formation of isatin. Indigo-red is also formed, but this may be titrated along with the indigotin by the permanganate. The method is better than the colorimetric processes in use.

J. J. S.

General and Physical Chemistry.

Fluorescence and Absorption Spectra of Sodium Vapour. R. W. WOOD and J. H. MOORE (*Phil. Mag.*, 1903, [vi], 6, 362—374).—The authors have investigated the fluorescence of sodium vapour with greatly improved apparatus and have obtained and examined photographs of the spectrum of the fluorescent light as well as the absorption spectrum, about 450 lines having been measured. The most interesting fact established is that the fluorescent spectrum is the exact complement of the absorption spectra, so that when the two were photographed on the same film either might have been a contact print taken from the other. Photographs and drawings are given in the paper. L. M. J.

Spectrum of Potassium. WALTER RITZ (*Ann. Physik*, 1903, [iv], 12, 444—446).—The author has shown that according to Kayser and Runge's formula there ought to be two potassium lines of wave-lengths 6936·4 and 6964·7 which had, however, not been observed previously. By using a six-prism instrument and volatilising potassium in an electric arc, the author has observed a new line of feeble intensity. Measurement of the wave-length gave 6964·4 ($\pm 0\cdot5$), which agrees well with one of the calculated values. J. McC.

Spark Spectrum of Radium. CARL RUNGE and J. PRECHT (*Ann. Physik*, 1903, [iv], 12, 407—412. Compare Abstr., 1900, ii, 641).—The spark spectrum of radium bromide has been observed with the aid of a Rowland diffraction grating. The wave-lengths and intensities of the various lines are noted and compared with those observed by Demarçay (Abstr., 1900, ii, 83) and others. The strongest lines can be grouped into three pairs. Certain of the lines (4726·9 and 4692·1) observed by Demarçay are certainly those of barium, and two bands (4627 and 4454) are due to his having used radium chloride, whereas the authors used bromide and did not find these. It may be confidently asserted that none of the strongest radium lines coincide with the solar lines measured by Rowland. J. McC.

Radioactivity of Metals Generally. J. C. McLENNAN and E. F. BURTON (*Phil. Mag.*, 1903, [vi], 6, 343—350).—It is found that a cylinder of any metal enclosed within, and insulated from, a second cylinder of the same material gradually acquires a negative charge and ultimately reaches a state of equilibrium in which its potential is lower than that of the enclosing cylinder. The experiments indicate that the most probable explanation lies in the supposition that an excess of positively charged corpuscles are emitted from the metal and that constancy is attained when the current between the cylinders counterbalances the loss of positive electricity. L. M. J.

Researches on Radioactive Substances. SKŁODOWSKA CURIE (*Ann. Chim. Phys.*, 1903, [vii], 30, 99—144).—A *résumé* of work already published (compare Abstr., 1900, ii, 81, 82, 83, 126, 654; 1901, ii, 216, 298, 589; 1902, ii, 190, 562). The author gives an historical account of radioactive substances, discusses the radioactivity of uranium and thorium, and describes what is known of polonium, radium, and actinium.

By fractionally crystallising ordinary barium chloride (50 kilos.), it has not been possible to separate any portion showing radioactivity.
J. McC.

Oxidising Action of the Rays from Radium Bromide as shown by the Decomposition of Iodoform. WILLIAM B. HARDY and Miss E. G. WILLCOCK (*Proc. Roy. Soc.*, 1903, 72, 200—204).—A solution of iodoform in chloroform rapidly becomes violet on account of the decomposition of the iodoform with liberation of free iodine. The decomposition only takes place if oxygen is present, but the amount necessary is exceedingly minute, and is induced by a radiant energy. The decomposition is accelerated by the presence of sodium chloride, potassium chloride, potassium nitrate, lead nitrate, barium nitrate, and barium chloride, but is retarded by potassium sulphate, calcium carbonate, barium sulphate, and magnesium carbonate; the influence of these salts seems to be a surface action entirely.

The influence of the radiations from radium bromide in promoting the decomposition has been studied. By suitably screening the tube containing the radium salt, it was found that the β rays are mainly effective in causing the decomposition, but the γ rays are also endowed with chemical activity. The Röntgen rays also cause the change to take place.

The authors conclude that the physiological action of radium rays is due to their power of penetration rather than to the fact that they exert any novel or very intense chemical action. They reach parts which are shielded by a cuticle very impervious to light waves, and in the subjacent tissues they induce some process of oxidation which does not take place without radiant energy.
J. McC.

Experiments in Radioactivity and the Production of Helium from Radium. Sir WILLIAM RAMSAY and FREDERICK SODDY (*Proc. Roy. Soc.*, 1903, 72, 204—207).—It has been proved that the inert gases of the air possess no inherent radioactivity, and the discharging power of air which has been noticed by many observers is caused by extraneous radioactivity.

The radium emanation withstands prolonged sparking with oxygen over alkali, and no effect is produced by passing it over a heated mixture of magnesium powder and lime. When the mixture with oxygen had been sparked for some time, the oxygen was withdrawn by means of phosphorus and no visible residue was left. But when another gas was introduced into the tube and then withdrawn, it was found to be radioactive.

The emanation from radium can be dealt with as a gas; it can be extracted by means of a mercury pump; it can be condensed in a U-tube in liquid air; when condensed, it can be washed

with another gas to which it communicates no radioactivity. The passage of the emanation through glass tubes can be seen in a dark room. When compressed, the luminosity is increased. The emanation causes the same chemical changes as the radium salt itself does. The emanation pumped off from 50 milligrams of radium bromide after dissolving in water, when stored with oxygen in a glass tube over mercury, turns the glass distinctly violet in a single night; if moist, the mercury becomes coated with a film of the red oxide, but if dry it is not attacked. A mixture of the emanation with oxygen produces carbon dioxide when passed through a lubricated stopcock.

The gas evolved from a solution of radium bromide consisted mainly of oxygen and hydrogen, which were removed, and the residue in a vacuum tube showed the spectrum of carbon dioxide. The vacuum tube was in communication with a U-tube, which was now cooled in liquid air, and this caused the brilliancy of the carbon dioxide spectrum to diminish, and at the same time the D_3 helium line appeared.

The emanation from radium bromide was conveyed by means of oxygen into a U-tube cooled in liquid air and the oxygen was then pumped out. The residue was washed with oxygen, then connected with a vacuum tube; the spectrum observed was a new one, probably that of the emanation, but after four days the tube showed the helium spectrum unmistakably.

J. McC.

Chemical Energy in Connection with the Phenomena Exhibited by Radium. NICOLAI N. BEKETOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 189—197).—The author considers that the atoms of the elements are formed by the condensation of a number of small particles of some primary material possessing a very large amount of energy, and that by such condensation, energy is lost, the loss becoming less as the amount of condensation increases. Some limit must exist to the condensation possible, and this seems to have been attained in the case of radium, which so readily decomposes. The decomposition of radium is paralleled by the auto-catalysis of endothermic compounds such as tellurium hydride and hydrogen peroxide, and also by the disintegration of metals by the electric current.

T. H. P.

Dependence of the Refractive Index of Gases on Temperature. GEORGE W. WALKER (*Phil. Trans.*, 1903, A, 201, 435—455).—With the aid of Jamin's interference method, the author has determined at various temperatures between 10° and 100° the index of refraction of air, hydrogen, carbon dioxide, ammonia, and sulphur dioxide; the values at *N.T.P.* are respectively 1.0002928, 1.0001407, 1.0004510, 1.0003793, 1.0006758. The temperature coefficients of the index of refraction for these five gases are respectively 0.00360, 0.00350, 0.00380, 0.00390, 0.00416, values which are less than those obtained by Mascart.

J. C. P.

Multirotation of Lactose. C. S. HUDSON (*Zeit. physikal. Chem.*, 1903, 44, 487—494).—Lactose exists in three modifications: (1) lactose hydrate, the specific rotation of which in freshly prepared solution is

about $+85^\circ$, subsequently falling to $+52.5^\circ$; (2) lactose anhydride, solutions of which cannot be distinguished from those of the hydrate; (3) lactose lactone, the specific rotation of which in freshly prepared solution is about $+35^\circ$, slowly rising to $+52.5^\circ$. The multirotation of lactose is attributed by the author to the gradual establishment of the equilibrium represented in the equation $C_{12}H_{24}O_{12}$ (hydrate) $\rightleftharpoons C_{12}H_{22}O_{11}$ (lactone) + H_2O .

Starting from this, the author deduces the relation $k+k' = 1/t \cdot \log(r_0 - r_\infty)/(r - r_\infty)$, where k and k' are the velocities of decomposition and formation of the hydrate; r_0 is the value of the rotation when all the sugar is present as hydrate, r is the value at time t , and r_∞ is the final value. The change of rotation is actually found to follow the course required by the above equation, and thus it is possible to get a definite numerical value for $k+k'$. If now the change of rotation is followed in a solution kept saturated with the hydrate, it is similarly possible to get a numerical value for k' . From these data, k/k' , that is, the equilibrium constant of the reaction, can be calculated. Hence, taking $+82.5^\circ$ as the specific rotation of the hydrate, and $+52.5^\circ$ as the final specific rotation of lactose, the author calculates the specific rotation of the lactone form as $+34^\circ$, in close agreement with actual observation.

Theoretically, $k+k'$ (that is, the velocity of multirotation) is the same whether a solution of the hydrate or one of the lactone is originally taken, a conclusion borne out by comparative experiments at several temperatures.

J. C. P.

Action of Inorganic Compounds on the Rotation of Quinic Acid. EBERHARD RIMBACH and PH. SCHNEIDER (*Zeit. physikal. Chem.*, 1903, 44, 467—486).—The results of the authors' investigations, which are of a preliminary character, are summarised as follows. The power of influencing to any noticeable extent the rotation of quinic acid is confined to members (1) of the carbon family, namely, titanium, zirconium, tin, and thorium; (2) of the oxygen family, namely, molybdenum, tungsten, and uranium. The oxygen derivatives of these elements, it is noted, are all of an acid character. As regards direction and extent of the above-mentioned influence, zirconium in particular is classed along with molybdenum, tungsten, and uranium, the elements which previous investigators have found specially efficient in increasing the rotation of oxy-acids. Comparison of the effects produced on the rotation of malic, tartaric, and quinic acids, shows that the increase of the rotation diminishes with the number of hydroxyl groups present in the molecule of the active acid. As in the case of other active oxy-acids, so in that of quinic acid, it has been frequently observed that the rotation reaches a maximum when the active acid and the stimulating inorganic compound are present in molecular proportions. The explanation of this is doubtless that complex molecules are formed with a higher rotation than the quinic acid itself. The rotation of quinic acid is only very slightly affected by the majority of inorganic compounds, and is nearly independent of the dilution.

J. C. P.

Effect of Pressure on Phosphorescing Sulphides. PERCY WAENTIG (*Zeit. physikal. Chem.*, 1903, 44, 499—500).—In reference to a recent paper by Tafel (*Ann. Physik*, 1903, 11, 3), the author records his observation that certain phosphorescent sulphides when ground in a mortar lose their power of phosphorescence, and at the same time assume another colour, the new colour being apparently complementary to that of the phosphorescence. If the powder is then heated to the temperature at which it was prepared, the phosphorescence and the original colour of the substance are fully restored.

J. C. P.

Relationships between Galvanic Elements with several Liquids. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 137, 285—290. Compare Abstr., 1902, ii, 375, 376, 439, 440, 546, 591; this vol., ii, 3, 258, 259, 464, 524, 525, 526).—In a cell composed of two liquids and two electrodes of different metals, if the *E.M.F.* of the system $M | A.B | M'$ is α_{AB} , and that of the system $M' | A.B | M$ is α_{BA} , the sum of these is equal to the sum of the *E.M.F.* of cells having each of the liquids separately, and in each case the two different electrodes. If the *E.M.F.* of the system $M | A | M'$ is represented by α_A , and that of the system $M | B | M'$ by α_B , then $\alpha_{AB} + \alpha_{BA} = \alpha_A + \alpha_B$. The metals used in the experimental verification of this deduction were zinc and copper, copper and platinum, and zinc and platinum; the liquids used were solutions of (1) zinc sulphate and boric acid, (2) sodium sulphate and boric acid, (3) sodium sulphate and sulphuric acid, (4) sodium sulphate and zinc sulphate, (5) sulphuric acid and boric acid, and (6) zinc sulphate and sulphuric acid.

If the *E.M.F.* of the system containing two liquids and the metals MM' be represented by α_{AB} , that with the metals reversed by α_{BA} , that with the metals MM'' by β_{AB} , and that with the metals MM'' by γ_{AB} , then it has been found that $\alpha_{AB} + \alpha_{BA} + \beta_{AB} + \beta_{BA} = \gamma_{AB} + \gamma_{BA}$.

Similar relationships can be established for cells containing more than two liquids. In the case of a system containing three liquids and two electrodes of the same metal, if the *E.M.F.* of $M | ABC | M$ is α_{ABC} , of $M | BAC | M$ is α_{BAC} , and of $M | ACB | M$ is α_{ACB} , and if the *E.M.F.* of the systems with two liquids are respectively α_{AB} for $M | AB | M$, α_{AC} for $M | AC | M$, and α_{BC} for $M | BC | M$, then $\alpha_{ABC} + \alpha_{BAC} + \alpha_{ACB} = \alpha_{AB} + \alpha_{AC} + \alpha_{BC}$. This is easily deduced by assuming that the effects which take place at the surfaces of contact of the liquids are related in the manner expressed by $AC + CB = AB$. The *E.M.F.* of systems containing several liquids and two electrodes of different metals can be connected in a similar manner with the *E.M.F.* of cells containing one liquid only: if an element consists of n liquids, $A_1, A_2, A_3, \dots, A_n$, and two electrodes of different metals, M and M' , then the number of systems which can be constructed by rearranging the liquids is represented by $1 \times 2 \times 3 \times \dots \times n$. The sum of the *E.M.F.* of these elements is connected with the *E.M.F.* of elements with a single liquid between the same electrodes by the formula:

$$\Sigma \alpha_{A_1 A_2 \dots A_n} = 1 \times 2 \times 3 \times \dots \times (n-1) (\alpha_{A_1} + \alpha_{A_2} + \dots + \alpha_{A_n}).$$

J. McC.

Remarks Concerning the Relationships between Galvanic Elements containing the same Liquids between Two Different or Identical Electrodes. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 137, 291—292. Compare preceding abstract).—The *E.M.F.* of cells with three liquids, two liquids, and one liquid between zinc and copper, between zinc and platinum, and between copper and platinum electrodes, and in the case of the three and two liquid elements with the electrodes reversed, have been determined. The solutions used were sodium sulphate, zinc sulphate, and sulphuric acid. The results show that the *E.M.F.* of cells with $\text{Zn} \mid \text{Cu}$ and $\text{Cu} \mid \text{Zn}$ electrodes are almost identical, in spite of the variation of the liquids in contact with each metal. The values are almost the same with these electrodes in elements with two liquids or elements with only one liquid, and this suggests that the *E.M.F.* is dependent only on the nature of the two metals. Comparison of the results obtained indicates that the variations of the *E.M.F.* found with the several electrodes depends on the heat of oxidation of the metals. Taken collectively, the results show that there is an essential difference between the *E.M.F.* of elements with different metals for electrodes and elements with two similar electrodes. In the latter case, the effect is due to the contact between a metal and two different liquids, but in the former case the effect is principally due to the opposition of the two metals. J. McC.

Galvanic Elements with Several Different Liquids and Identical Metallic Electrodes. MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1903, 137, 421—430. Compare this vol., ii, 524).—The *E.M.F.* of elements containing the same metal (zinc, copper, or platinum) as electrodes and several liquids in porous cells have been determined. In the first case, the terminal liquids were solutions of normal salts (zinc sulphate and sodium sulphate), and other salt solutions, acids, or alkalis were interposed between these. In all cases, the difference of potential was very small. In some instances, where several liquids were interposed, practically no *E.M.F.* was obtained, but this does not indicate that there is no potential difference at the surfaces of contact of the various liquids, but only that the final effect is the result of compensation.

When the terminal liquids are solutions of an acid and of a normal salt, the *E.M.F.* is low if the acid is a weak one like boric acid, but it is comparatively high if sulphuric acid is used, and particularly with platinum electrodes. The *E.M.F.* does not remain constant for any length of time, because by diffusion, sulphuric acid gets into the other solutions and very greatly modifies their properties from an electromotive point of view.

With an alkali solution for one terminal liquid, and a normal salt solution for the other, the *E.M.F.* is comparatively high, and almost the same for a two-liquid cell as when other solutions are interposed between these liquids. The high *E.M.F.* is attributed to the special electrochemical relationship between metallic oxides and alkalis; with respect to acids and normal salts, the metal (zinc, copper, platinum) oxides are electropositive, but with reference to alkalis they are electro-

negative, and these two influences acting on the two electrodes will tend to establish a considerable potential difference.

A high *E.M.F.* is also produced when the terminal liquids are solutions of an acid and of an alkali, and the *E.M.F.* is almost the same with salt solutions interposed, as when only the two liquids are used.

The author discusses shortly the seat of energy in the various galvanic elements described by him. J. McC.

Chemical Potential and Electromotive Force. WILDER D. BANCROFT (*J. Physical Chem.*, 1903, 7, 416—427).—The author states that the paper is chiefly based on a letter from Gibbs. In a system in which there is a flux of electricity, the equation for equilibrium is $(V'' - V') + a_a(\mu'' - \mu' - \phi'' + \phi') = 0$, where V'' , V' are the electrical potentials of pieces of the same kind of metal connected with the electrodes, ϕ' , ϕ'' are the gravitational potentials assumed to be uniform, μ' , μ'' are the intrinsic potentials, and a_a is Maxwell's electrochemical equivalent. From this, neglecting the gravitational potentials and assuming Avogadro's law to hold in the solution, is deduced for a cell with concentration electrodes $(V'' - V') = a_a(B + AT \log \gamma_a / M_a - \mu''_a)$, where γ_a is the density of a component, and M_a its molecular weight, B depends on solvent and temperature. This may be written $V'' - V' = a_a AT / M_a \log(\gamma_a / G)$, similar to the Nernst expression, but has the advantage of bringing out the fact that G (the solution pressure of Nernst's formula) is a function of at least three variables, electrode, solvent, and temperature. Other formulæ of Nernst and Planck, as, for example, those applied in the case of cells with electrolytes of different concentration, are also deducible from the fundamental equation. L. M. J.

Laws Governing Electric Discharges in Gases at Low Pressures. W. R. CARR (*Phil. Trans.*, 1903, A, 201, 403—433).—Paschen has found that with spherical electrodes and a given spark potential the gaseous pressure at which an electric discharge occurs is inversely proportional to the distance between the electrodes. The author, using parallel plate electrodes in a uniform field, extends the application of the above law to a number of gases (air, hydrogen, and carbon dioxide) for pressures at, and below, the critical pressure (this being the pressure for which the spark potential has its minimum value). The values of the spark potentials were for all pressures, independent (1) of the size of the electrodes, provided the discharge took place in a uniform field; (2) of the material of the electrodes, iron, zinc, aluminium, and brass being used in turn. Paschen's law appears to be applicable so long as the distance between the electrodes is greater than the diameter of the sphere of molecular action. The minimum spark potential varies with different gases, but is a constant for a given gas, independent alike of the gaseous pressure and of the distance between the electrodes. From the author's results it seems that the minimum spark potential is a property of the atom rather than of the molecule; for any selected gas its value may be calculated additively.

J. C. P.

Do the Ions carry the Solvent with them in Electrolysis?
 CORNELIS A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 97—99).—The electrolysis of a solution of silver nitrate in a mixture of methyl alcohol and water was carried out between silver electrodes. After the electrolysis, the solutions at the cathode and at the anode were analysed. No change in the concentration of the methyl alcohol could be detected, although the method adopted was sufficiently accurate. The result, therefore, indicates that there is no migration of solvent molecules with the ions, although it is possible that the two ions act in a similar manner and carry equal quantities of one or both of the solvents, but in opposite directions. J. McC.

Colour of Ions. AL. PFLÜGER (*Ann. Physik*, 1903, [iv], 12, 430—438).—The absorption of solutions of permanganates and of solutions of salts of *p*-rosaniline have been quantitatively determined, and Ostwald's statement that "the spectra of dilute solutions of different salts with the same coloured ion are identical" has been fully confirmed. The absorption of the permanganate solutions examined was in all cases the same, although the dissociation was not complete. J. McC.

Stability of Salts with Oxidisable Cathions and Anions.
 RICHARD ABEGG (*Zeit. Elektrochem.*, 1903, 9, 569—572).—The tendency of an element of valency n in contact with a solution containing its own ions in concentration c to take up a positive charge of electricity is measured by its electrolytic potential $E_0 - 0.058/n \log c$. The tendency of an ion of a lower degree of oxidation to take up a positive charge and so pass into an ion of a higher degree of oxidation may be measured in volts in a similar way. The author shows how the stability of a salt, in aqueous solution, is connected with these electrolytic (or oxidation) potentials. The following is an example of the method employed, which is applied to a number of well known cases. The tendency of a ferric ion to lose a positive charge and so to pass into a ferrous ion in a solution containing $[\text{Fe}^{+++}]$ and $[\text{Fe}^{++}]$ gram-molecules of ferric and ferrous ions per litre is $0.71 + 0.058 \log [\text{Fe}^{+++}]/[\text{Fe}^{++}]$ volts. The tendency of an iodine ion to lose a negative charge (or, what comes to the same thing, to take up a positive charge) and so change into neutral iodine is $-0.52 + 0.058 \log [I']$ volt. In a solution containing ferrous, ferric, and iodine ions, equilibrium will be attained when the tendency of the ferric ions to lose positive charges is equal to that of the iodine ions to take up positive charges, that is, when $0.71 + 0.058 \log [\text{Fe}^{+++}]/[\text{Fe}^{++}] = -0.52 + 0.058 \log [I']$ or, when $[\text{Fe}^{+++}][I']/[\text{Fe}^{++}] = 1/1900$. Chemically, this means that ferric iodide can only exist in solution in presence of an enormous excess of ferrous iodide, or if iodine ions (potassium iodide, for example) are added to a ferric salt, the greater part of the latter is reduced to ferrous salt and the iodine ions are converted into free iodine. A similar calculation for bromine gives $[\text{Fe}^{+++}][\text{Br}']/[\text{Fe}^{++}] = 76000$, which shows that ferric bromide is quite stable. T. E.

Electrolytic Conductivity of Solutions of Sodium in Mixtures of Ethyl or Methyl Alcohol and Water. S. TYMSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 104—107).—The con-

ductivity of solutions of sodium in different mixtures of ethyl alcohol and water and methyl alcohol and water have been determined at 18°. The two alcohols behave differently; in the case of ethyl alcohol, the change of conductivity with varying composition of the solvent is quite regular, but with methyl alcohol a minimum is reached. This minimum is dependent on the dilution of the solution as well as on the composition of the solvent; it occurs when there is about 80 per cent. of methyl alcohol present, but only becomes evident when the dilution is greater than 8 litres.

The minimum occurs in the neighbourhood of these dilutions at which it has been found (Steger, *Abstr.*, 1899, i, 745; Lobry de Bruyn and Steger, *ibid.*) that a maximum reaction velocity is produced in the substitution of a nitro-group by an alkoxy-group in aromatic compounds.

J. McC.

Electrochemistry of the Compounds of Iodine and Oxygen. I and II. ERICH MÜLLER (*Zeit. Elektrochem.*, 1903, 9, 584—594 and 707—716).—The author applies Luther's theory of the relation between the *E.M.F.* corresponding with the conversion of the lowest, intermediate, and highest stages of oxidation of a substance into each other (*Abstr.*, 1900, ii, 705, and 1901, ii, 301) to the reactions (1) $I' + 4H_2O + 8F \rightleftharpoons IO_4' + 8H'$; (2) $I' + 3H_2O + 6F \rightleftharpoons IO_3' + 6H'$; (3) $IO_3' + H_2O + 2F \rightleftharpoons IO_4' + 2H'$. In alkaline solutions containing the substances in normal concentration, the *E.M.F.* found at platinised electrodes, compared with the normal hydrogen electrode, are 0.227 volt for (2) and 0.513 volt for (3), from which the value 0.2986 volt is calculated, by Luther's formula, for reaction (1), whilst the value found by experiment is 0.387 volt. A graphical representation of the influence of the concentration of the ions on the *E.M.F.* of the reactions is given, and this is used, in conjunction with the above values, to deduce the behaviour of acidified solutions of the different iodine compounds.

The second part of this communication contains a graphical method of representing the changes of free energy which accompany the reactions between the different stages of oxidation of iodine. An interesting conclusion is drawn that, "A lower and a higher stage of oxidation can only react to form a given intermediate stage when all the reactions leading to the other intermediate compounds are accompanied by a loss of free energy." A case in point is the reaction between periodate and iodine ions to form iodate. This does not take place in alkaline solutions, probably because the reaction of these substances to form another intermediate compound (free iodine) is accompanied by gain of free energy. In acid solutions or in presence of platinum black, or in light or at higher temperatures, this is no longer the case, and the reaction takes place.

T. E.

Anode Potentials in the Formation of Lead Carbonate and Chromate. GERHARD JUST (*Zeit. Elektrochem.*, 1903, 9, 547—549).—When a solution containing sodium chlorate and carbonate is electrolysed with a lead anode, the potential at the anode sometimes increases gradually by more than 1 volt (the current being kept

constant). The author finds that the lower potential is that of lead in a solution containing bivalent lead ions, whilst the higher potential is that of lead peroxide, but the potential difference between a lead anode and a solution containing bivalent lead ions depends very much on the anodic current density (probably owing to local increase of the concentration of the lead ions), so that at high current densities it may rise to the normal value for lead peroxide. When this is the case, lead peroxide is, of course, formed on the anode. In the solutions containing chlorate and carbonate, the skin of lead carbonate formed on the anode (Abstr., 1902, ii, 442) diminishes its effective surface and so increases the current density until the potential rises to the value at which lead peroxide is formed.

T. E.

Electrolysis of Fused Lead Chloride with Reference to its Connection with Current Density and Current Yield. A. APPELBERG (*Zeit. anorg. Chem.*, 1903, 36, 36—75).—In continuation of the work of Helfenstein (Abstr., 1900, ii, 383) and Auerbach (Abstr., 1901, ii, 590), the author has determined the current yield and studied the phenomena which occur at the cathode and at the anode in the electrolysis of fused lead chloride. The arrangement was similar to that used by Helfenstein, and the fused lead chloride was contained in a V-tube. The results (exhibited in tables and graphically) which are obtained with varying current density show that as the density decreases the yield of lead diminishes regularly. If the current yield curve be extrapolated, it meets the current strength axis at about 0.05 ampere; therefore, if the current strength is reduced below this, no lead is separated. The minimum current intensity corresponding with this point is about 0.6 volt, but these values are not absolute, since they vary with the conditions of the experiment, such as temperature and distance between the electrodes. With high current densities, the polarisation is almost constant at 1.25 volts, and is independent of the density.

The chlorine yield was determined by Auerbach's method, using varying current density. With high densities, the yield agrees with the lead yield, but with low densities, the agreement is not good, and this is to be attributed to variation of the experimental conditions.

The electrolysis takes place in a cylindrical vessel standing either vertically or obliquely, just as in the V-tube; in all cases, the current yield is independent of the duration of the electrolysis.

When a cylindrical cell was used, a cloud of lead was always produced in the lead chloride; in order to avoid this, a current of chlorine was passed through the fused mass, but this was not successful and it lowered the current yield.

In the electrolysis of a eutectic mixture of lead chloride and potassium chloride (mixture in molecular proportions, melting point about 430°), no lead cloud is formed; as the solubility of lead in this mixture is low and as a comparatively low temperature can be used, it has been found that at high current densities Faraday's law is obeyed, even when no special arrangement is adopted for separating the electrodes. The eutectic mixture of lead chloride and sodium chloride (about $2\text{PbCl}_2 + \text{NaCl}$, melting point 440°) behaves in quite the same

way. Addition of ferric chloride to the fused lead chloride diminishes the yield of lead; 0.1 per cent. of ferric chloride diminishes the yield to 76.8 per cent., and when 2 per cent. of ferric chloride is present the yield is only about 20 per cent.

RICHARD LORENZ has developed the formula $a = 100 - (k/i^n)$ to express the course of the curves obtained; a is the percentage current yield, k and n are constants, and i is the current strength. J. McC.

Decompositions in Potassium Cyanide Silver Baths. EDUARD JORDIS and WILHELM STRANER (*Zeit. Elektrochem.*, 1903, 9, 572—575).—The decompositions in three electroplating baths were studied. Two of these contained a solution of silver cyanide in potassium cyanide; one of them was used for plating, whilst the other remained idle; the third bath contained a solution of silver chloride in potassium cyanide. All the baths lost cyanogen, the working baths more quickly than the idle one and the chloride bath more quickly than the other. The amount of carbonate increased most rapidly in the working baths, which points to anodic oxidation of cyanide; this was most marked in the chloride bath. The loss of cyanide was greater, however, than can be accounted for by the increase of carbonate; after several months' work, oxalic and acetic acids were found to be present. The common statement that new silver baths give bad results is quite devoid of foundation. T. E.

Reaction Acceleration and Retardation in Electrical Reductions and Oxidations. RUDOLF RUSS (*Zeit. physikal. Chem.*, 1903, 44, 641—720).—The depolarisation caused by nitrobenzene, *p*-nitrophenol, sodium hypochlorite, and quinhydrone with gold, platinum, silver, iron, and nickel electrodes has been determined; the first two substances were examined in acid and in alkaline solutions. The strongest influence is exerted by gold and the least by nickel. The material of the electrode is not constant in its action; by prolonged cathodic polarisation, it can be rendered more active, but this activity is of an unstable nature.

In those cases where the depolarisation is good, the concentration-potential curve is very regular and represents a logarithmic function. According to the nature of the electrode, the accelerating or retarding action of the metal is indicated by the curve. The total effect must be regarded as the sum of two separate effects—the nature of the metal used and its particular state of activity at the time. These two effects may be in the same or in opposite directions so far as the reduction or oxidation is concerned. J. McC.

On the Possible Forms of the Melting Point Curve for Binary Mixtures of Isomorphous Substances. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 151—169).—A mathematical paper in which it is proved that in the curve representing the melting points of binary mixtures of isomorphous substances an interruption may occur. In this connection, it is necessary to remember that unstable phases may occur, particularly in the solid condition, and in all cases it is possible to trace the melting point curve through the eutectic point.

The author shows that the occurrence of a eutectic point and the apparent interruption in the series of solid mixtures caused by it necessarily follow when the heat required for the mixing of the solid phase is high and thus causes unstable conditions. In reality, the curve is continuous, but as a rule only a part of the continuous curve above the eutectic point can be experimentally determined.

J. McC.

The Specific Heat of Solutions of Naphthalene in Various Organic Solvents. The Heat Change arising from the Dissolution of Naphthalene in various Solvents. CARL FORCH (*Ann. Physik*, 1903, [iv], 12, 202—210; 211—217).—The specific heats of solutions of various concentrations of naphthalene in chloroform, carbon disulphide, toluene, benzene, and ether have been determined. When the results are plotted graphically, it is found that the specific heat of the solutions varies almost rectilinearly with the concentration. From the results, the specific heat of naphthalene has been calculated and found to be about 0.354, although the value from the solutions in ether is 0.427. The specific heat of solid naphthalene is about 0.32 and that of liquid naphthalene is 0.41, therefore naphthalene dissolved in carbon disulphide, toluene, benzene, or chloroform has a specific heat just a trifle higher than that of solid naphthalene, whilst in ethereal solution its specific heat approaches that of naphthalene in the liquid state.

The heat of solution of naphthalene in the same solvents has also been determined. In toluene, benzene, or chloroform, the heat of solution is independent of the dilution; in carbon disulphide, it is a trifle higher at higher concentrations, and in ether there is a decided increase in the heat of solution as the concentration rises. The heats of solution determined were: 35.04 cal. in carbon disulphide, 32.60 cal. in toluene, 32.26 cal. in benzene, 27.04 cal. in chloroform, and 28.07 cal. in ether at 1.63 per cent., and 29.26 cal. at 8.44 per cent. The heat of fusion of naphthalene is 35.6 cal. and agrees with the heat of solution in carbon disulphide. There is a difference between the heat of fusion and heat of solution in toluene and benzene, and a greater difference in the cases of chloroform and ether. J. McC.

Determination of Specific Heats, especially at Low Temperatures. H. E. SCHMITZ (*Proc. Roy. Soc.*, 1903, 72, 177—193).—The following specific heats have been determined:

	<i>a.</i>	<i>b.</i>	<i>c.</i>		<i>a.</i>	<i>b.</i>	<i>c.</i>
Copper.....	0.0800	0.0793	0.0936	Nickel.....	0.0843	0.0823	0.1094
Thallium....	0.0301		0.0326	Cobalt.....	0.0843	0.0837	0.10795
Lead	0.0294	0.0300	0.03046	Zinc.....	0.0839	0.0849	0.0931
Aluminium	0.1724	0.1735	0.21825	Silver	0.0514	0.0519	0.0559
Cast Iron	0.0893		0.1189	Tin	0.0498	0.0508	0.0552

The results given under *a* were found between the temperature of liquid air and the ordinary temperature by the method of mixture. Those given under *b* were obtained by determining the weight of ice which was formed on a cylinder of the metal after it had been cooled

in liquid air and then immersed in water. Under *c*, the results obtained between 100° and 20° by the method of mixture are given.

Comparing these results, it is seen that the proportional alteration of specific heat is relatively large for metals of low atomic weight. Consequently, the approximate constancy of atomic heat for the higher temperature range is not preserved for the lower temperature range, and, in fact, for the metals examined at the lower range there is a progressive rise of atomic heat with atomic weight. J. McC.

Thermochemical Studies of Colouring Matters. Rosaniline and Pararosaniline. JULES SCHMIDLIN (*Compt. rend.*, 1903, 137, 331—334).—The heats of neutralisation of rosaniline and pararosaniline have been determined; on account of the low solubility, it was only possible to carry out the determinations with dilute solutions of acids. It was found that, besides the thermal change due to neutralisation, another heat change, sometimes negative and sometimes positive, takes place, which is accompanied by either a development or a destruction of colour. This second phenomenon is probably due to hydration or dehydration. The dissolution of the base of rosaniline in acetic acid is accompanied by two superposed thermal changes which take place at different speeds. The observed effects were: $C(C_6H_4 \cdot NH_2)_3 \cdot OH$ (colourless) + $C_2H_4O_2 = C(C_6H_4 \cdot NH_2)_2(OH) \cdot C_6H_4 \cdot NH_2 \cdot C_2H_4O_2$ (colourless) + 7.87 Cal., and $C(C_6H_4 \cdot NH_2)_2(OH) \cdot C_6H_4 \cdot NH_2 \cdot C_2H_4O_2$ (colourless) = $H_2O + C(C_6H_4 \cdot NH_2)_2 \cdot C_6H_4 \cdot NH_2 \cdot C_2H_4O_2$ (coloured) - 3.39 Cal.

With hydrochloric acid, the reaction is different, because a coloured solution is first formed on dissolving the mono- or tri-hydrochloride in this acid, and the product then becomes hydrated to yield a colourless carbinol derivative. The following table gives the heats of neutralisation of the salts of rosaniline and pararosaniline:

Monohydrochlorides.		Pararosaniline.	Rosaniline.
Base dissolved in ($HCl + 100H_2O$)...	+ 18.53 Cal.	+ 18.75 Cal.	
Dissolved hydrochloride	8.39 "	8.66 "	
<hr/>		<hr/>	
Solid base + HCl (solution) = solid hydrochloride + H_2O	10.14 "	10.13 "	
Trihydrochlorides.			
Hydrochloride dissolved in ($HCl + 100H_2O$)	8.39 "	8.66 "	
Dissolved trihydrochloride.....	1.99 "	2.31 "	
<hr/>		<hr/>	
Solid hydrochloride + $2HCl$ (solution) = solid trihydrochloride	6.35 "	6.40 "	
Sulphates.			
Base dissolved in ($H_2SO_4 + 200H_2O$)	21.20 "	21.51 "	
Sulphate	10.58 "	10.92 "	
<hr/>		<hr/>	
Solid base + $\frac{1}{2}H_2SO_4$ (dissolved) = solid sulphate + H_2O	10.62 "	10.59 "	

Acetates.	Pararos-aniline.	Rosauiline.
Base dissolved in 2·7 per cent. acetic acid	+ 5·19 Cal.	+ 5·43 Cal.
Dissolved acetate	1·33 „	1·59 „
Solid base + $C_2H_4O_2$ (dissolved) = solid acetate + H_2O	3·86 „	3·84 „
Oxalates.		
Base dissolved in ($HCl + 100H_2O + \frac{1}{2}C_2H_2O_4$)	19·70 „	19·67 „
Oxalate dissolved in ($HCl + 100H_2O$)	12·43 „	12·74 „
Solid base + $\frac{1}{2}C_2H_2O_4$ (dissolved) = solid oxalate + H_2O	7·27 „	6·93 „
		J. McC.

Lowering of the Freezing Point of Aqueous Hydrogen Peroxide by Sulphuric and Acetic Acids. HARRY C. JONES and GRANTLAND MURRAY (*Amer. Chem. J.*, 1903, 30, 205—209. Compare Jones, Barnes, and Hyde, *Abstr.*, 1902, ii, 203; Jones and Carroll, this vol., ii, 131).—Sulphuric acid produces a much greater lowering of the freezing point of hydrogen peroxide than of water, and the molecular lowering is greater the more concentrated the solution of hydrogen peroxide. The freezing point of water is lowered by acetic acid to an extent which corresponds approximately with the slight dissociation of the acid, whilst the freezing point depressions in the case of hydrogen peroxide are somewhat greater than with water. Sulphuric and acetic acids seem, therefore, to undergo greater electrolytic dissociation in hydrogen peroxide than in water. A. McK.

New Laws of Tonometry which can be Deduced from Raoult's Experiments. E. WICKERSHEIMER (*Compt. rend.*, 1903, 137, 319—322).—Starting with the Clapeyron and Clausius' equation, the author mathematically deduces that the expenditures of heat necessary to separate from a solution the same quantity of the solvent either in the solid or the gaseous state, are in the proportion of the squares of the absolute freezing and boiling points. From Raoult's law, it is deduced that whatever be the substance (non-electrolyte) dissolved in a given solvent, the density of the saturated vapour of the solution is constant, that is to say, it is independent of the nature and weight of the dissolved substance when the solution is a dilute one.

The author further shows that the coefficient adopted should be 1·98335 instead of 1·988. J. McC.

The Boiling Point Curves of the System: Sulphur—Chlorine. H. W. BAKHUIS ROOZEBOOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 63—66).—The vapour pressure and the boiling point curves of mixtures of sulphur and chlorine have been determined. In the liquid state, these elements are miscible in all proportions. When the results

are represented graphically, the liquid curve and the vapour curve very nearly meet at a point corresponding with the composition of the mixture $S + Cl$. The fact that they do not quite meet indicates that the compound formed, S_2Cl_2 , is not perfectly stable either in the liquid or gaseous condition, but undergoes a slight dissociation.

The curves obtained for mixtures lying between Cl_2 and $S + Cl$ differ according to the time which has elapsed between preparing the mixture and making the determination. When the mixture is obtained from liquid chlorine and liquid S_2Cl_2 , it remains yellow for a long time if the temperature is kept below 0° , but at higher temperatures it quickly becomes red owing to the formation of $SOCl_2$, and at the same time there is a diminution of volume. The presence of this more highly chlorinated compound so modifies the vapour pressure and boiling point curves for mixtures richer in chlorine than $SOCl_2$ that they lie nearer together.

J. McC.

Relation between Trouton's Formula and Van der Waals' Equation. A. A. BRANDT (*J. Russ. Phys. Chem. Soc.*, 1903, 35, ii, 417—420).—As has been pointed out by Guldberg, the ratio between the absolute boiling point and the absolute critical temperature is, for most substances, constant and equal to 0.6. By applying this relation to Van der Waals' equation, the author derives Trouton's formula, the constant of which is calculated to be 10.8; this is only about half the experimental constant, which varies between 20 and 22.

T. H. P.

Vapour Densities of some Carbon Compounds; an Attempt to Determine their Exact Molecular Weight. Sir WILLIAM RAMSAY and BERTRAM D. STEELE (*Zeit. physikal. Chem.*, 1903, 44, 348—378).—The carbon compounds studied are methyl alcohol, ether, benzene, toluene, hexane, *n*-octane, and β -dimethylhexane, which were all carefully purified. A weighed quantity of each substance was taken, and its vapour density determined in an apparatus similar in principle to that used by Gay-Lussac. The pressure under which the volume of vapour was measured could be varied, so that its compressibility could be ascertained within certain limits. For very low pressures, the compressibility was determined with an apparatus previously constructed by one of the authors (*Trans.*, 1902, 81, 1176). The determinations of the vapour density were further made at three temperatures, 100° , 115° , and 130° , obtained by surrounding the vaporisation tube with the vapour of chlorobenzene, boiling under suitable pressure. Oxygen was taken as the standard of comparison, but instead of finding its density directly at the above-mentioned temperatures, the authors determined its coefficient of expansion between 0° and 130° ($=0.0036694$), and used the figure 1.42961 as the weight in grams of 1 litre of oxygen at 0° , this number being based on the work of Regnault, Jolly, Leduc, and Rayleigh.

The authors' experimental results are summed up in a number of curves, obtained by plotting PV/T against P for each temperature. An extrapolation to $P=0$ then gives the value of the vapour density under zero pressure. It is found that the differences between the

values so found for the molecular weight and the values obtained by taking the sum of the atomic weights of the constituent elements are too great to be accounted for by the experimental errors of the method, which have been carefully estimated. Determinations with different samples of hexane, benzene, ether, and toluene show that the discrepancies cannot be attributed to the impurity of the materials used. The authors discuss several other possible causes, but these are all regarded as inadequate.

J. C. P.

Determinations of Molecular Weights at very High Temperatures. WALTHER NERNST (*Zeit. Elektrochem.*, 1903, 9, 622--628).—Victor Meyer's displacement method is used, the tube consisting of pure iridium. Owing to the extreme difficulty of working this material, the volume of the bulb is only about 2.5 c.c. In order to weigh the minute quantities of material required, a special balance was constructed on the torsion principle. A thin glass rod was fastened to a quartz fibre stretched horizontally. One end of the glass rod was used as a pointer, the position of which was read on a glass scale. The apparatus is heated in an iridium tube, coated externally with magnesia and asbestos, and heated by means of an electric current. The temperature was measured photometrically by comparing the emission of the heated tube with a standard source of light. Since the different parts of the interior of the tube are all at the same temperature, its radiation is the same as that of a black body, and its temperature may be calculated. The air displaced by the vapour is measured by the displacement of a thread of mercury in a calibrated capillary tube. The upper part of the apparatus is cooled by a spiral of copper tubing through which water circulates, so that by rubber connections it may be connected to the glass capillary tube and to the arrangement for introducing the weighed substances.

The evaporation of the substances, when dropped into the hot tube, usually takes place so rapidly that a little of the vapour is driven up into the cold upper part of the apparatus; the volume of air displaced is therefore usually rather too small and the molecular weight calculated too high.

The following are the results obtained :

Substance.	Temp.	Mol. weight.	Substance.	Temp.	Mol. weight.
Carbon dioxide ...	1973°	42.1—44.3	Sulphur.....	1690°	59
Mercury	1952	201.0—205.0	„	1808	54
Water	1973	17.1—18.4	„	1820	48
Sodium chloride ...	1973	53.1—63.3	„	1930	54
Potassium chloride	1980	81.8—85.9	„	1998	44
			„	2023	54

The experiments with sulphur were made in an atmosphere of nitrogen. When sulphur was introduced into the tube containing air no change of volume took place, which shows that sulphur dioxide is not dissociated at 1950°. At the same temperature, silver was not volatile.

The higher figures in the above table were always obtained with

the larger amounts of substance owing to the larger quantity of vapour driven into the cold part of the apparatus. The values for sulphur are also too high on account of the polymerisation of the sulphur vapour in the cooler parts of the tube. T. E.

Critical Density. ISIDOR TRAUBE (*Zeit. Elektrochem.*, 1903, 9, 619—620).—A number of small glass bulbs of known densities are sealed up in a glass tube with chloroform. Even at 10° above the critical temperature, the bulbs remain floating at different levels for hours, indicating differences of density in the contents of the tube of more than 50 per cent. The author interprets this experiment by supposing that the vapour and liquid consist of molecules of different sizes; at the critical temperature the two become completely miscible, but not identical. T. E.

Pressure Curves of Univariant Systems which contain a Gas Phase. ALBERT BOUZAT (*Compt. rend.*, 1903, 137, 322—324. Compare this vol., ii, 529, 588).—The ratio of the temperatures (absolute) at which the vapour pressures of the system are 900 mm. and 300 mm. respectively has been determined. The systems all contain one gas phase and are divided into four groups; the first group (solid \rightleftharpoons liquid + gas) is represented by chloroform hydrate and chlorine hydrate; the second group (solid \rightleftharpoons solid + gas, or solid \rightleftharpoons gas) is represented by $\text{NH}_4\text{Cl}, 3\text{NH}_3-3\text{ZnCl}_2, 6\text{NH}_3$, and ammonium carbamate; the third group (liquid \rightleftharpoons gas) is represented by chlorine—fluorobenzene and acetone; and the fourth group (liquid \rightleftharpoons solid + gas) is represented by $\text{NH}_4\text{NO}_3, \frac{3}{2}\text{NH}_3-\text{SeO}_2, 2\text{HCl}$ and $\text{NH}_4\text{I}, 3\text{NH}_3$. The following law is found to apply to all four groups: the ratio of the absolute temperatures corresponding with the same pressure in any two systems whatever of the same group is constant whatever be the pressure chosen. This law may also be expressed as follows: the variation of entropy which results from the liberation of a molecule of gas under a definite pressure has the same value for all systems of the same group. But the variation of entropy which results from the liberation of a molecule of gas from a solid or from a liquid under a definite pressure decreases from group 1 to group 4. J. McC.

Association of a Liquid Diminished by the Presence of another Associated Liquid. HARRY C. JONES and GRANTLAND MURRAY (*Amer. Chem. J.*, 1903, 30, 193—205).—The connection between the association of a solvent and its dissociating power has been expressed by Dutoit and Aston (*Abstr.*, 1897, ii, 546), whilst Jones and Lindsay (this vol., ii, 55) have proved that the electrical conductivity of a salt in mixed solvents, such as water, methyl, ethyl, and propyl alcohols, is often smaller, for a definite concentration, than in the less conducting of the two solvents present in the mixture; it was accordingly assumed that the dissociating power of one solvent is influenced by the presence of the other.

To determine the mutual influence of associated liquids on each other's association, molecular weights of each associated liquid in the other have been determined by the cryoscopic method and the results

compared with the molecular weights of each individual liquid. The substances used were water, acetic acid and formic acid; these liquids dissolve readily in one another without chemical interaction, do not undergo much electrolytic dissociation, and are strongly associated.

Formic acid, after purification by distillation over phosphoric oxide and fractional solidification of the product, was found to solidify at 7° .

The association of water is greatly diminished by acetic acid. In the most dilute solutions, the molecular weight is slightly greater than the molecular weight corresponding with H_2O , whilst in the most concentrated solutions the value is a little greater than that corresponding with $(\text{H}_2\text{O})_2$. Ramsay and Shields have shown that in pure water the molecules correspond with the composition $(\text{H}_2\text{O})_4$. The effect of formic acid on the association of water is similar, the associated molecules of water being broken up even to a greater extent than with acetic acid. The association of acetic acid is greatly diminished by water. In the other cases examined, it is also shown that the associated molecules of the dissolved substance are broken down by the solvent into simpler molecules; the numerical data of the investigation are tabulated and curves are given showing the variation of molecular weight with concentration.

The experiments of Jones and Lindsay (*loc. cit.*) are interpreted in the light of the preceding results.

A. McK.

Variation of the Absorption Coefficient of Ammonia in Water by the Addition of Carbamide. FRANZ GOLDSCHMIDT (*Zeit. anorg. Chem.*, 1903, 36, 88—91. Compare Abstr., 1902, ii, 15).

—The value of $\lambda'^2.p.[\text{H}_2\text{O}]/\lambda^2.p'.[\text{H}_2\text{O}]'$ obtained from the previous results should be equal to 1, but it is actually found to be inconstant, and to vary from 1.28 to 1.44. The cause of this deviation is discussed, and it is concluded that it is due to the variation of the absorption coefficient due to the added carbamide. The relative lowering of the solubility of ammonia by carbamide is found to be about $0.22(1/n[1-l'/l])$, where l is the absorption coefficient in water at 25° , and l' is the absorption coefficient in a carbamide solution of normality n . This lowering has not previously been recognised for non-electrolytes. The relative lowering is independent of the concentration of the ammonia and of the carbamide.

J. McC.

Velocity of Transformation of Carbon Monoxide. II. ANDREAS SMITS and LUDWIG K. WOLFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 66—72. Compare this vol., ii, 276).—By the method previously used, it has been proved, with pumice-nickel-carbon as catalyst, that at 445° the conversion of carbon monoxide into carbon dioxide and carbon is a unimolecular reaction, contrary to Schenk and Zimmermann's statement (this vol., ii, 423) that it is a bimolecular one. No satisfactory reaction constant could be obtained at 445° , and this was proved to be due to the fact that at this temperature the reaction is reversible, although Boudouard (Abstr., 1901, ii, 646) has stated that at 445° carbon monoxide can be completely decomposed into carbon and carbon dioxide. Starting with carbon dioxide in the reaction vessel at 445° , it was found that after prolonged heating carbon monoxide was formed, but the same equilibrium could not be

attained as when the experiment was carried out with carbon monoxide.

Even on using a catalyst obtained by reducing nickel oxide with hydrogen, it has not been found possible to verify Schenck and Zimmermann's results, and no explanation can be offered of why they obtained results leading to the conclusion that the reaction is a bimolecular one.

J. McC.

Kinetics of the Reaction between Carbon Monoxide and Oxygen. HANS KÜHL (*Zeit. physikal. Chem.*, 1903, 44, 385—459).—The velocity of this reaction at 570° has been determined by tracing the gradual diminution of pressure accompanying the combination of the two gases. The results obtained were somewhat irregular, for although the reaction in general appeared to be of the third order, the velocity varied according as one or other of the gases was first introduced into the reaction vessel, which was made of internally glazed porcelain. Thus the initial velocity when dry oxygen is added to moist carbon monoxide is ten times greater than that observed when moist carbon monoxide is added to dry oxygen, carbon dioxide being originally present in both cases; when carbon dioxide has not been previously introduced, the velocities in question are in the ratio 2:1. The initial velocity is in general retarded when carbon dioxide is originally present; it is in the main independent of the oxygen concentration, but proportional to the first power of the carbon monoxide concentration; it increases with the amount of water vapour present, although somewhat irregularly, and to a less than proportional extent. Further, the initial velocity is increased when the reaction vessel has been previously exhausted.

In some cases, where the results obtained were not in agreement with the formula for a termolecular reaction, an empirical formula was found more satisfactory. In accounting for the influence of water vapour on the reaction, the author refers to the view advocated by Dixon and L. Meyer, who suggested that the union of carbon monoxide and oxygen really took place in two stages: (a) $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$; (b) $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. The author now, assuming that (b) takes place much more rapidly than (a), deduces a theoretical expression which has a marked formal resemblance to the empirical expression referred to above. Neither, however, is satisfactorily in accord with all the experimental results.

The paper contains also a new mode of arriving at the theoretical equation for the velocity of a reaction of the third order, in the special case where the reacting substances are present in equivalent quantity.

J. C. P.

The Rate of Formation of Sulphur Trioxide in Presence of Platinum. GUIDO BODLÄNDER and K. KÖPPEN (*Zeit. Elektrochem.*, 1903, 9, 559—568).—Mixtures of dry sulphur dioxide, oxygen, and nitrogen in different proportions are admitted into a vacuum tube containing platinum, and heated at a constant temperature. The volume of the enclosed gas is maintained constant, the progress of the reaction being observed by means of the change of pressure. Platinised

asbestos cannot be used, since asbestos is attacked by sulphur trioxide; platinum wire gauze was therefore employed. Since the dissociation of sulphur trioxide is not perceptible below 430° , the velocity of the reaction may be taken to be proportional to the product of some power of the concentration of the sulphur dioxide and of the oxygen. The results are, on the whole, in fair agreement with the requirements of the equation for a reaction of the third order— $dc/dt = K(C_{\text{SO}_2})^2(C_{\text{O}_2})$. The effect of temperature is to increase the velocity of the reaction 1.4 to 1.5 times for each 10° rise of temperature. The values of K at any temperature should be unaffected by the addition of an indifferent gas to the mixture; this is, however, not the case. The addition of nitrogen to a mixture of 2 volumes of sulphur dioxide and 1 volume of oxygen accelerates the reaction in such a way that the percentage of the sulphur dioxide which is converted into sulphur trioxide in a given time is independent of the quantity of nitrogen added. No explanation of this deviation from the theory is attempted.

The rate of formation of sulphur trioxide is increased by adding sulphur dioxide or oxygen in excess, but not so much as the theory of reaction velocity would lead one to expect. The reaction has a measurable velocity at 100° .
T. E.

Velocity of Transformation of Persulphuric Acid into Caro's Acid, and the Formula of the Latter. MARTIN MUGDAN (*Zeit. Elektrochem.*, 1903, 9, 719—721).—The velocity of transformation of persulphuric acid, dissolved in a large excess of sulphuric acid, into Caro's acid is proportional to the concentration of the persulphuric acid. The velocity constants increase with the concentration of the sulphuric acid. The addition of potassium sulphate diminishes the velocity. To decide between the formulæ proposed for Caro's acid (H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_9$), the author has used the reaction with potassium iodide; a substance having the first formula would react thus, $\text{H}_2\text{SO}_5 + 2\text{KI} = \text{K}_2\text{SO}_4 + 2\text{I} + \text{H}_2\text{O}$, whilst one having the second formula would give $\text{H}_2\text{S}_2\text{O}_9 + 4\text{KI} = 2\text{K}_2\text{SO}_4 + 4\text{I} + \text{H}_2\text{O}$. Twice as much iodine is formed for each equivalent of acid which disappears in the second case as in the first. The author's results are in good agreement with the second formula, and he therefore gives to Caro's acid the formula $\text{H}_2\text{S}_2\text{O}_9$, this being identical with the formula adopted by Armstrong and Lowry (*Abstr.*, 1902, ii, 558).
T. E.

Determination of the Viscosity of Phenol in the Liquid State. O. SCARPA (*Nuovo Cimento*, 1903, [v], 5, 117—130).—The author has determined the viscosity of phenol at different temperatures by means of Poiseuille's apparatus, the results obtained leading to the following conclusions: the variation of the viscosity of phenol with the temperature proceeds regularly and without singular points down to the temperature of spontaneous crystallisation, that is, to below the temperature corresponding with its melting point. As is the case with hygroscopic substances, Graetz's relation between internal friction and critical temperature is not applicable to phenol. Neither Graetz's formula nor any other of those proposed represents the viscosity of phenol when it is completely liquid.
T. H. P.

Relation between Stefan's Formulæ for the Internal Pressure of Liquids and Van der Waals' Equation. A. A. BRANDT (*J. Russ. Phys. Chem. Soc.*, 1903, ii, 409—415).—The author shows that the formulæ given by Stefan (Abstr., 1887, 323) for the internal pressure of liquids can be easily deduced from Van der Waals' equation, and hence merit attention in the consideration of the connection between the theories of vaporisation and capillarity.

T. H. P

Initial Acceleration in Chemical Change. VICTOR H. VELEY (*Phil. Mag.*, 1903, [vi], 6, 271—279).—When the rate of a chemical change is low at first, rises gradually to a maximum, and finally falls off in accordance with the law of mass action, the phenomenon may be attributed either (1) to the formation up to a certain point of some accelerating substance, or (2) to the formation and retention up to a certain point of an intermediate or final reaction product, this being responsible for a delay. Examples of these two categories are discussed in the paper. The following actions are classed under the first head:—the formation of nitrous acid when certain metals are acted on by dilute nitric acid; the formation of persulphuric acid when zinc is acted on by dilute sulphuric acid; the production of manganese sulphate in the reaction between permanganate and oxalic acid; the formation of monosymmetric sulphur in the conversion of rhombic sulphur into that modification; the formation of cyamelide in the polymerisation of cyanic acid. Under the second category are classed the following:—the formation of an unstable bromo-addition product in the bromination of organic acids; the decomposition of ammonium nitrite in aqueous solution; the evolution of carbon monoxide from formic and sulphuric acids (about 80°); the decomposition of ammonium nitrate (about 190°). In the last two actions, with which the author deals more particularly, he shows that if allowance is made for the retention up to a certain point of the gaseous products of reaction, the course of the decomposition can be accurately predicted with the help of Esson's hypothesis.

J. C. P.

Gelatinisation. II. S. A. LEVITES (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 253—263. Compare Abstr., 1902, ii, 312).—The author has investigated the influence of the presence of a number of different electrolytes and non-electrolytes on the rapidity of gelatinisation of agar-agar and gelatin solutions.

For gelatin solutions, the results are briefly as follows: (1) aqueous solutions of salts of monobasic acids retard gelatinisation, whilst salts of di- or poly-basic acids cause an acceleration. Hence the action depends mainly on the anion, the part played by the cation being much less striking. Exceptions are met with in the case of the salts of the fatty acids; thus the alkali salts of the first two acids of this series produce acceleration where retardation of the gelatinisation would be expected, but the salts of the alkaline earth metals cause retardation. (2) Monohydric alcohols diminish the rate of gelatinisation, the effect increasing as the molecular weight of the alcohol

increases. (3) Polyhydric alcohols hasten gelatinisation. (4). Aldehydes, with the exception of formaldehyde, which may enter into combination with the gelatin, retard gelatinisation. (5) Carbohydrates (sucrose) cause a slight increase in the rate of gelatinisation.

Variations from the above rules occur in the case of solutions of agar-agar. Thus chlorides, bromides, or cyanides accelerate gelatinisation; otherwise, the action of salts of monobasic acids as well as of di- and poly-basic acids is the same as with gelatin.

In the majority of cases, the results show that, both with gelatin and agar-agar, the amount of the acceleration or retardation is proportional to the quantity of electrolyte or non-electrolyte present. The main exception to this rule is found in the case of the alcohols. T. H. P.

Apparatus for the Purification of Gases. HENRI MOISSAN (*Compt. rend.*, 1903, 137, 363—369).—It has been found that gases may be desiccated by passage through tubes immersed in refrigerating liquids; thus moist air, after passage through tubes cooled to -50° , was so dry that the moisture contained in 3 litres of it produced no measurable increase in the weight of a drying-tube through which it was finally passed.

Experiments have shown that whilst in the case of a heavy gas such as carbon dioxide it is possible to rapidly sweep out the contained air from a generating apparatus so that the fourth litre collected contains only 0.8 per cent. of air, in the case of a lighter gas, such as ammonia, this degree of purity was only attained after collecting 8 litres.

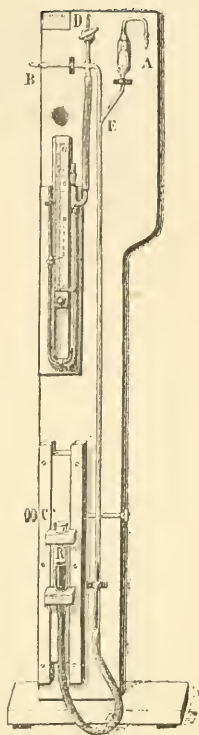
With readily liquefiable gases, it is shown to be unnecessary to free the generating flask, delivery tubes, &c., from air before collecting the gases, since these can be solidified by passage through cooled vacuum tubes.

The apparatus used for the preparation of pure, dry gases, on the principles indicated above, is figured in the original paper, and consists of the usual generating apparatus communicating with a series of three desiccating tubes of special patterns immersed in suitable volatile liquids boiling between -200° and -30° , a three-way tap in communication with (a) a mercury manometer and (b) a condensing vessel of special form, which is connected to a mercury pump. The gas produced is liquefied, and finally solidified in the condensing tube; communication with the generating apparatus is then stopped, and the remainder of the apparatus exhausted; finally, the condenser is allowed to regain the ordinary temperature and the gas is collected in the usual way, fractionation being resorted to if necessary.

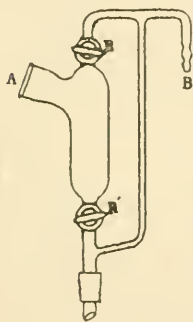
This method has been successfully employed in the preparation of carbon dioxide, hydrogen iodide and chloride, nitric oxide, and other gases. T. A. H.

Apparatus for the Liquefaction of Hydrogen. KARL OLSZEWSKI (*Bull. Acad. Sci. Cracow*, 1903, 241—246. Compare this vol., ii, 203).—The apparatus is in principle the same as that recently described, but the regenerators have now been arranged more compactly, being entirely enclosed in a single large vacuum vessel. Only 1700 grams of liquid air were found necessary for the production of 200 c.c. of liquid hydrogen. A drawing of the apparatus, with details of the construction and method of working, are given in the paper. C. H. D.

Regulator for Fractional Distillation under Reduced Pressure. GABRIEL BERTRAND (*Bull. Soc. chim.*, 1903, [iii], 29, 776—778).—The regulator is practically a kind of barometer composed of a vertical tube, the lower part of which communicates with a small mercury reservoir which may be raised or lowered as required, whilst the top is bent at right angles and connected with the distilling apparatus. At a height of 750 mm., the vertical tube is sealed to a side tube fitted with a mercury trap which communicates with an air-pump or exhauster. The pressure, which is read off on a syphon-barometer, is regulated by moving the mercury reservoir in a vertical direction as required. When the mercury reaches the side tube, the communication between the pump and the distilling apparatus is stopped, and remains so while the pressure is constant. L. DE K.



Separator for Fractional Distillation under Reduced Pressure. GABRIEL BERTRAND (*Bull. Soc. chim.*, 1903, [iii], 29, 778—779).—The apparatus consists essentially of a cylindrical separating funnel



furnished with a side inlet tube connected with the distilling apparatus. The stem of the separating funnel is fitted below the tap with a side-tube leading to the pump and joining another tube communicating with the upper end of the funnel, which may also be closed by means of a tap. The fractions are collected in flasks attached to the stem by means of the indiarubber stopper. During the distillation, the taps are opened, and when the receiver has to be changed they are momentarily closed (compare Thorne, *Trans.*, 1883, 43, 301). L. DE K.

A New Refrigerator. BRACONNIER and G. CHATELAIN (*Bull. Soc. chim.*, 1903, [iii], 29, 779—780).—The apparatus resembles that of Allihn and Béal, the condensing tube being furnished with four bulbs, but it has also a double water circulation. The vapours pass through the annular space between two cold surfaces and meet with a succession of spaces alternately widened and narrowed; this prevents the vapours from forming a cylindrical column, which would be cooled only at its circumference. L. DE K.

Wash-bottle and Safety-tube. H. VIGREUX (*Bull. Soc. chim.*, 1903, [iii], 29, 841—843).—The apparatus consists of a glass tube, closed at the upper end by a cork, enlarged into a cylindrical bulb below the centre, and terminating in a pear-shaped bulb, through the apex of which penetrates a glass tube of narrower bore open at both ends, reaching almost to the cork, and serving as an exit tube.

The pear-shaped bulb further carries the entrance tube, which is a lateral U-tube having one large and two small bulbs on its outer and longer limb. The washing liquid occupies the lateral tube from the centre of the longer limb, and also fills the pear-shaped bulb of the main tube. The apparatus can be used in the reverse direction as a safety tube.

T. A. H.

Inorganic Chemistry.

The Isotherm of the Dissociation of Sulphur at 448°. GERHARD PREUNER (*Zeit. physikal. Chem.*, 1903, 44, 733—753).—The author shows that a satisfactory explanation of the results obtained by Biltz and Preuner (*Abstr.*, 1902, ii, 132) on the gas density of sulphur at 448° under different pressures from 10 mm. to 500 mm. is that besides the molecules S_8 and S_2 there are also S_6 and S_4 molecules present. This is deduced from the course of the curve representing the change of gas density with change of pressure.

The author has also calculated the equilibrium constants from the experimental data, and thus the whole course of the dissociation is known.

J. McC.

Action of Phosphonium Iodide on Polychlorides. ERNESTINE FIREMAN and PETER FIREMAN (*Amer. Chem. J.*, 1903, 30, 116—133).—Phosphorus chloronitrides are formed when phosphorus pentachloride is heated with ammonium chloride, and the action of phosphonium iodide on polychlorides was therefore investigated with the object of preparing analogous phosphorus compounds. Phosphonium iodide reacts readily on heating with phosphorus or antimony pentachloride or with tin tetrachloride. Reduction of the polychloride takes place with formation of the lower chlorides and iodides, hydrogen chloride being evolved and a part of the phosphorus being set free in the amorphous form. The course of the reaction was determined quantitatively in each case, and is represented by the equations: $3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + 2P$; $3PCl_5 + 3PH_4I = PCl_3 + PI_3 + 12HCl + P$; $6SnCl_4 + 6PH_4I = 3SnCl_2 + 3SnI_2 + 18HCl + 2PH_3 + 4P$.

C. H. D.

Molecular Compounds of Iodine. D. STRÖMIHOLM (*Zeit. physikal. Chem.*, 1903, 44, 721—732).—The saturation concentration of iodine over free iodine and over the periodide, NMe_4I_9 , has been determined in pure solvents and in solvents containing the substance which is being examined as to its capability of forming an additive compound with iodine. The experiments were made with ether, carbon disulphide, ether and water, and ether and water containing sodium sulphate. The addition of water to ether causes an increase in the saturation concentration of the iodide, the increase being greater over the periodide than over free iodine. The increase over pure iodine is almost exactly proportional to the concentration of the water in the

ether, but the increase is much more rapid when the periodide is used for the saturation.

Experiments were also made with mixtures of alcohol and ether, alcohol and carbon disulphide, ether and carbon disulphide, chloroform and ether, chloroform and carbon disulphide, benzene and ether, and methyl iodide and ether. The increased solubility in those solvents to which water had been added can be explained by the formation of iodine hydrates, and similar increases were observed where alcohol and ether were used, thus indicating that molecular compounds are formed also with these. It is to be observed that these are the solvents in which iodine dissolves with a brown colour, and in those solvents in which iodine dissolves with a violet or red colour no evidence of the formation of additive compounds could be found. J. McC.

Arsenic in Sea-water, Rock Salt, Table Salt, Mineral Water, &c., and its Estimation in some Common Reagents. ARMAND GAUTIER (*Compt. rend.*, 1903, 137, 374—375).—The author corrects certain results given in milligrams instead of thousandths of a milligram, recorded in his previous paper on this subject (this vol., ii, 593). The water of the Atlantic Ocean in the neighbourhood of the Azores is now shown to contain at depths of 10, 1335, and 5943 metres respectively 0.025, 0.010, and 0.080 milligram of arsenic per litre. Specimens of sodium chloride of the following origins, (*a*) the coast of Brittany, (*b* and *c*) Olonne sands, (*d*) commercial so-called "English" salt, contained respectively 0.003, 0.001, 0.045, and 0.015 milligram of arsenic in 100 grams.

Specimens of rock salt from Stassfurt, Saint Nicolas (near Nancy), Djebel-Amour, and Mount Vesuvius contained respectively 0.0025, 0.014, 0.005, and 0.175 milligram of arsenic in 100 grams. A sample of salt of unknown origin contained, after fusion at a red heat, 0.030 milligram in 100 grams. T. A. H.

Decomposition of Potassium Chlorate, with some Observations on the Decomposition of Sodium Chlorate and Perchlorate. JON SCOBAL (*Zeit. physikal. Chem.*, 1903, 44, 319—347).—The chief reaction involved in the decomposition of potassium chlorate at 395° is represented by the equation $4\text{KClO}_3 = 3\text{KClO}_4 + \text{KCl}$, but there occurs simultaneously a secondary reaction, represented by the equation $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$. The temperature 395° was chosen for the study of these reactions after it had been shown that the perchlorate is not appreciably decomposed at 390°, 395°, or 411°. The course of the decomposition was followed quantitatively, and it was found that the primary reaction at 395° is quadrimolecular, whilst the secondary reaction is unimolecular. The decomposition of potassium chlorate in fused potassium nitrate as solvent was also studied at 410°, at which temperature potassium nitrate itself is stable and has no action on potassium chloride or perchlorate. In this case also, the course of decomposition is represented by the two parallel reactions referred to above.

The behaviour of sodium chlorate under the action of heat is

analogous to that of potassium chlorate. Sodium perchlorate, like other perchlorates, decomposes into chlorate, chloride, and oxygen.

J. C. P.

A Double Salt of Potassium and Barium Nitrates. WILLIAM K. WALLBRIDGE (*Amer. Chem. J.*, 1903, 30, 154—156).—A double salt of the formula $2\text{KNO}_3 \cdot \text{Ba}(\text{NO}_3)_2$ is obtained on evaporating concentrated solutions of potassium and barium nitrates, in fairly large, opaque, tetrahedral crystals, resembling impure barium nitrate, but giving very constant results on analysis. Other double salts of barium and the alkali metals are unknown.

C. H. D.

Preparation of Alkali Metals. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 140737).—Alkali fluorides or silicofluorides are heated with metallic aluminium, when the alkali metal distils off and is collected. The reaction proceeds according to the equation $6\text{KF} + \text{Al} = 3\text{K} + \text{K}_3\text{AlF}_6$. The operation is free from danger.

C. H. D.

Preparation of Sodium Oxide. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 142467).—When potassium nitrate is heated with metallic potassium, potassium peroxide is formed, sodium nitrate or nitrite, on the other hand, is decomposed by metallic sodium into sodium oxide, free from peroxide, according to the equations $5\text{Na} + \text{NaNO}_3 = 3\text{Na}_2\text{O} + \text{N}$ and $3\text{Na} + \text{NaNO}_2 = 2\text{Na}_2\text{O} + \text{N}$. The nitrite is to be preferred, as the reaction is more under control and the iron vessel is less attacked. Should the product contain any unaltered sodium and sodium nitrate, it is again heated to incipient fusion in a closed crucible.

C. H. D.

Reduction of Metallic Oxides in a Current of Hydrogen. FERDINAND GLASER (*Zeit. anorg. Chem.*, 1903, 36, 1—35).—The oven in which the metallic oxide was heated consisted of a magnesia tube heated at a constant temperature by a wire spirally wound round it and through which a current was passed. The tube was supported centrally in a glass tube narrowed at one end and was insulated by asbestos and loose magnesia. The temperature used was up to about 500° and was measured by a platinum—platinum-rhodium couple. The hydrogen was carefully purified and the formation of water was detected by allowing the gas to pass over a small cylinder of dried cobalt chloride. It was estimated that 0.15 milligram of water is sufficient to cause the blue cylinder to appreciably change colour.

The reduction of the metallic oxide begins at a definite temperature, and the following table gives the temperature for the various oxides:

Silver.	Ag_2O	34°	Nickel.	Ni_2O_3	188°	Manganese.	MnO_2 ...	185°
	Ag_2O	63		Ni_3O_4	198		Mn_2O_3 ...	230
Copper.	CuO (from			NiO	230		Mn_2O_4 ...	296
	nitrate) .	150		Ni_2O	339		MnO	1300
	(powdered)	199	Cobalt.	Co_2O_3	182	Zinc.	ZnO	454
	Cu_2O	155		Co_3O_4	207	Mercury.	HgO (yel-	
Lead.	PbO_2	189		CoO	228		low) ..	75
	PbO	211	Iron.	Fe_2O_3	287		(red)	140
	Pb_2O	235		Fe_3O_4	305			
Cadmium.	CdO	282		FeO	370			

In the cases of metals with several stages of oxidation, it was found that the higher oxide is always reduced at a lower temperature than the lower oxide.

With silver oxide, it was found that there is no catalytic influence exerted on the combination of a mixture of hydrogen and oxygen.

The reduction of a metallic oxide at a definite temperature may serve as a method of preparing lower oxides in some cases, and this method may also be adopted for the estimation of the quantities of the components of a mixture of oxides. At 300° , when a mixture of copper oxide and zinc oxide is heated in a current of hydrogen, only the copper oxide is reduced, and from the loss in weight the quantity of copper oxide originally present can be calculated. At 260° , only the copper oxide in a mixture of this with ferric oxide is reduced. In a mixture of copper oxide and nickel oxide, only the copper oxide is reduced if the temperature is not too high, and when a mixture of silver oxide and copper oxide is treated at 120° , only the silver oxide is reduced.

J. McC.

A Peculiar Property of some Hydrated Salts. AUGUST DE SCHULTEN (*Bull. Soc. chim.*, 1903, [iii], 724—726).—Although the hydrated magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, and arsenate, $\text{Mg}_3(\text{AsO}_4)_2 \cdot 22\text{H}_2\text{O}$, lose 18 and $17\text{H}_2\text{O}$ respectively at 100° , the less hydrated salts, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, are stable at this temperature; the manner in which water is lost in the case of these salts is thus quite exceptional, the octohydrates retaining more water at 100° than that which remains in the products formed on heating the hydrates with $22\text{H}_2\text{O}$ at the same temperature (compare this vol., ii, 655).

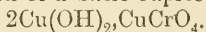
W. A. D.

Precipitation of Calcium and Magnesium by Sodium Carbonate. JOHN M. STILLMAN and ALVIN J. COX (*J. Amer. Chem. Soc.*, 1903, 25, 732—742).—The presence of sodium chloride was found to have no important influence on the precipitation of dilute calcium chloride solution by sodium carbonate. Sodium carbonate was added to magnesium chloride solutions in presence of sodium chloride and sodium sulphate respectively, when the latter exerted a greater influence in preventing precipitation than an equivalent amount of the former. The influence of temperature in cases of solutions of magnesium chloride and sodium carbonate, alone and in presence of sodium sulphate and sodium chloride respectively, has been studied and the results graphically depicted.

A. McK.

Cupric Chromate. MAX GRÜGER (*Monatsh.*, 1903, 24, 483—497).—The action of cupric chloride on potassium chromate in aqueous solution leads to the formation of a voluminous, rusty-brown precipitate, which, when left in contact with excess of cupric chloride solution, becomes dark red and thus has the composition of *basic potassium cupric chromate*, $\text{KCu}_2(\text{OH})(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$, and consists of stellate aggregates of thin, four-sided prisms. When fused, it blackens and evolves oxygen; the residue yields potassium chromate and

dichromate on extraction with water. When boiled with water, it is decomposed with formation of a basic cupric chromate,



The rusty-brown precipitate first formed contains a larger proportion of potassium and yields the same basic cupric chromate when boiled with water.

Cupric sulphate and potassium chromate in aqueous solution yield an amorphous, rusty-brown precipitate which becomes crystalline when left in contact with excess of the copper salt solution. The precipitate is basic potassium cupric sulphato-chromate, the proportion of sulphate present depending on the concentration of the copper salt solution and the duration of its contact with the precipitate. The double salt is rapidly decomposed either by boiling water or by fusion, but without formation of potassium chromate. The same precipitate is obtained on adding potassium hydroxide to the mixture of cupric sulphate and potassium dichromate in aqueous solution (compare Knop, *Annalen*, 1848, 70, 52). Addition of sodium chromate to cupric chloride in aqueous solution results in the formation of a greenish-yellow precipitate which, when left in the mother-liquor, gradually assumes a bright rusty-brown colour, but does not become crystalline. The greenish-yellow substance is the basic cupric chromate, $2\text{Cu}(\text{OH})_2, \text{CuCrO}_4$; the rusty-brown precipitate contains a larger proportion of chromic acid, which is removed by washing with water, the greenish-yellow salt being regenerated.

In the action of ammonium chromate on cupric sulphate, Balbiano's results are confirmed (Abstr., 1888, 1249), but it is considered that the original precipitate contains ammonium, whilst the basic salt $2\text{Cu}(\text{OH})_2, \text{CuCrO}_4$ is formed as the result of washing the insoluble substance with boiling water.

G. Y.

Silver Iodide-nitrate and Silver Iodide. RICHARD FANTO (*Monatsh.*, 1903, 24, 477—482).—The double salt, $\text{AgI}(\text{AgNO}_3)_2$, formed in Zeisel's methoxy-determination, is obtained in small, glistening needles if the methyl iodide current is slow and largely diluted with carbon dioxide. When dry, the salt is perfectly white and melts at $118\text{--}119^\circ$; it is not sensitive to light when preserved in dry air and is very easily decomposed by water or alcohol. The double salt obtained by fusing 1AgI with 2AgNO_3 melts at the same temperature and has the same properties (Risse, *Annalen*, 1859, 111, 39).

In its behaviour towards light, silver iodide obtained from the double salt is similar to that obtained by precipitation. The specific gravity of silver iodide, as given by previous authors, varies between 5.02 and 5.91. Silver iodide, formed in the cold, contracts when warmed from -10° to $+70^\circ$ and expands again on cooling (Fizeau, *Compt. rend.*, 1867, 64, 314, 771). Silver iodide, when prepared at 100° or when heated to 100° after formation, does not exhibit these changes in density, and has a higher sp. gr., namely, 5.79, than the salt prepared at the ordinary temperature, which is found to have a sp. gr. 5.66.

G. Y.

Complex Haloid Salts of Mercury. MILES S. SHERRILL (*Zeit. Elektrochem.*, 1903, 9, 549—554. Compare this vol., ii, 534).—The haloid salts of mercury form complex ions with the halogens (X) having the general formula $(\text{HgX}_2)_m(\text{X}')_n$, which are partially dissociated in aqueous solution. The dissociation constant

$$K_1 = [(\text{HgX}_2)_m(\text{X}')_n] / [\text{HgX}_2]^m [\text{X}']^n,$$

where the square brackets indicate the concentrations of the substances within them, and also the values of m and n can be calculated when the concentrations are known. The concentration of the free mercuric haloid is obtained by means of the coefficient of partition between the aqueous solution and benzene or ether. The ratio of the concentrations of the mercuric ions in two solutions is obtained from measurements of the *E.M.F.* of concentration cells with mercury electrodes. Since the concentration of the mercuric ions in a normal calomel electrode is calculated from the results of Ogg (*Abstr.*, 1899, ii, 14) and Abel (*Abstr.*, 1901, ii, 376) to be 5.3×10^{-20} gram-molecules per litre, the actual concentrations in the other solutions can be obtained. This method is limited to small concentrations of the mercuric salts (except in the case of the cyanide), because they are reduced to mercurous salts by the mercury electrode in more concentrated solutions.

The elevation of the freezing point of a solution of a haloid salt of an alkali metal by the addition of the corresponding mercury salt and the increase in the solubility of the mercury salts in such solutions are used to confirm the results obtained by the two first methods.

The following solubilities are given in gram-molecules per litre at 25°:

	$\text{Hg}(\text{CN})_2$.	HgI_2 .	HgBr_2 .	HgCl_2 .
Water	0.44	0.00013	0.017	0.263
Benzene	very small	0.00493	0.0194	0.0197
Ether	0.010			

The coefficients of partition for water : benzene are : HgI_2 , 1 : 38 ; HgBr_2 , 1 : 1.12 ; HgCl_2 , 1 : 0.075. The coefficient for $\text{Hg}(\text{CN})_2$ in water and ether is 44 : 1.

When the concentration of the mercuric salt is small or the excess of halogen ions is very large, complex ions of the type $m=1$, $n=2$ are formed with all four mercury salts, but when their concentration increases, other more complicated ions are formed, the exact nature of which is not known so certainly as that of the simpler type found in the dilute solutions.

When mercuric cyanide is added to a solution containing cyanogen ions, the very stable complex ion $\text{Hg}(\text{CN})_2(\text{CN}')_2$ is formed quantitatively so long as any free CN' ions remain; after this, further addition of mercuric cyanide leads to the ion $\text{Hg}(\text{CN})_2(\text{CN}')$. These appear to be the only complex ions formed by mercuric cyanide. In the more concentrated solutions of the remaining salts, indications were found of the existence of the following ions: $(\text{HgCl}_2)_2(\text{Cl}')_2$, $(\text{HgCl}_2)_3(\text{Cl}')_2$, $(\text{HgBr}_2)_2(\text{Br}')_2$, and $(\text{HgI}_2)_2(\text{I}')_3$.

For the numerical values of the dissociation constants of the

complex ions and of the mercury haloid salts, the original must be consulted.

T. E.

Atomic Weight of Lanthanum. HARRY C. JONES (*Zeit. anorg. Chem.*, 1903, 36, 92—99. Compare Abstr., 1902, ii, 563).—The author replies to Brauner's criticism (*Zeit. anorg. Chem.*, 1903, 33, 317) of atomic weight determination by synthesis of the sulphate of a metal, and insists that the method is in some cases quite admissible. The author points out that the lanthanum oxide previously used by him was found to be pure spectroscopically, whereas the material employed by Brauner and Pavliček (*Trans.*, 1902, 81, 1243) was not thus examined. The results obtained by Brauner and Pavlicek for the atomic weight of lanthanum are higher by about 0.25 than those found by the author, and the high result is attributed to the imperfect method of heating the oxide. The atomic weight determination by converting the oxide into sulphate has been repeated, and the mean value found is 138.80, which is in good agreement with the value previously obtained (138.77). In this case, as before, the lanthanum oxide was heated in a porcelain crucible placed within a platinum crucible, and under such circumstances it remains perfectly white. Brauner's method of heating the oxide in a platinum crucible was tried, and the atomic weight obtained from the result was 139.02 when the heating was continued for 1 hour, and 139.07 when the heating was continued for 5 hours. After heating the oxide in a platinum vessel and then heating it in a current of hydrogen, a loss in weight of about 0.2 per cent. could be observed; apparently when lanthanum oxide is heated in contact with platinum a small quantity of a peroxide is formed; that some change takes place is shown by the substance becoming slightly brown.

J. McC.

Permanent Protection of Iron and Steel. MAXIMILIAN TOCH (*J. Amer. Chem. Soc.*, 1903, 25, 761—766).—Experiments on the protective influence of Portland cement on iron and steel are quoted. If a proper cement paint is applied to a surface which has begun to oxidise, further oxidation will be arrested. If the cement used is very fine and free from iron, calcium sulphate, and sulphides, it will quickly set, and, when thoroughly applied, it may be painted with adherent paint. Free lime on the surface of the cement coating has no injurious action on linseed-oil paint.

A. McK.

Diagram showing the Properties of Nickel Steels. LÉON GUILLET (*Compt. rend.*, 1903, 137, 411—413. Compare this vol., ii, 297, 483).—The author indicates graphically the percentage of carbon on the abscissa-axis, and that of nickel on the ordinate, and has obtained four lines converging at 1.65 per cent. of carbon on the axis, and starting respectively at 10, 13, 25, and 29 per cent. of nickel. These lines divide the space into five fields corresponding with definite structures of the steels. The first field represents steels of the same structure as ordinary carbon steel. The second corresponds with steel consisting of α -iron and martensite, the third with pure martensite, the fourth with martensite and γ -iron, and the fifth with

γ -iron. By means of the diagram and the composition of a nickel steel, it is possible to deduce its structure and consequently its mechanical properties. J. McC.

The Condition of Hydrates of Nickel Sulphate in Methyl Alcohol Solution. CORNELIS A. LOBRY DE BRUYN and C. L. JUNGUS (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 91—94).—By determining the rise of boiling point of methyl alcohol when water is added, it was found that the elevation (0.281° for 1 per cent. of water) is quite normal, and no minimum boiling point is obtained as with ethyl alcohol and water. The rise of boiling point of methyl alcohol, in which the nickel sulphates, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 3\text{H}_2\text{O} \cdot 3\text{MeOH}$, were dissolved, was determined, and this increment was employed in calculating how much water was absorbed by the alcohol from the hydrated salt. The results show that only one molecule of water is retained by nickel sulphate when dissolved in methyl alcohol.

The authors conclude that, in aqueous solutions, salt molecules are combined with water molecules, and that hydrates are already present in the solutions from which they crystallise. J. McC.

The Conductive Power of Hydrates of Nickel Sulphate dissolved in Methyl Alcohol. CORNELIS A. LOBRY DE BRUYN and C. L. JUNGUS (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 94—97).—The conductivity of solutions of the various hydrates of nickel sulphate in methyl alcohol has been determined at 18° for different dilutions. By carrying out the determination immediately after preparing the solution and again after some delay, the fact was established that a stationary condition is set up as soon as dissolution takes place, although in some instances lower hydrates or alcohol-hydrates only separate after some time.

With nickel sulphate, the conductivity diminishes as the dilution increases until at a dilution of 128 litres a minimum value is obtained. Further dilution causes an increase in the conductivity, but even at a dilution of 4096 litres no maximum value has been obtained. The conductivity is very small compared with that of salts with univalent ions in the same solvent and with aqueous solutions of salts generally. J. McC.

Double Carbide of Chromium and Tungsten. HENRI MOISSAN and A. KOUZNETZOW (*Compt. rend.*, 1903, 137, 292—295).—*Chromium-tungsten carbide*, $\text{CW}_2 \cdot 3\text{C}_2\text{Cr}_3$, is formed by heating a mixture of chromic oxide, tungstic acid, and carbon in a carbon crucible in the electric furnace for 5 minutes with a current of 400 amperes at 75 volts, and treating the product with warm hydrochloric acid, then with concentrated ammonia solution. It can also be formed by heating chromium, tungsten, carbon, and copper in a carbon crucible, and dissolving the copper from the product with nitric acid. The double carbide is obtained in small, hard, crystalline grains. It has a sp. gr. 8.41 at 22° and is not magnetic. It is attacked by chlorine at 400° , bromine only slowly acts on it at 500° , and at this temperature it is not affected by iodine. When heated in the air, it does not inflame,

and at a red heat sulphur does not attack it. It is not attacked by any acid or mixture of acids. Although attacked only slowly by fused potassium hydroxide or alkali carbonates, it is rapidly decomposed by fused alkali nitrates or potassium chlorate, giving a mixture of chromate and tungstate. When heated in hydrogen chloride, chromic chloride, tungsten chloride, hydrogen, and methane are formed. By the addition of tungsten to chromium steels, the formation of this stable, hard carbide might give rise to the production of new steels with special qualities.

J. McC.

Manganic Periodates. W. B. PRICE (*Amer. Chem. J.*, 1903, 30, 182—184).—When manganese sulphate (or nitrate) is dissolved in a large excess of dilute sulphuric acid (or nitric acid) and then mixed with a sulphuric acid (or nitric acid) solution of sodium or potassium periodate or of periodic acid, the substances, to which the compositions $\text{Na}_2\text{Mn}_2\text{I}_2\text{O}_{11}$, $\text{K}_2\text{Mn}_2\text{I}_2\text{O}_{11}$, and $\text{H}_2\text{Mn}_2\text{I}_2\text{O}_{11}$ are assigned, are respectively precipitated as bright red powders. They are remarkably stable in the absence of reducing agents.

A. McK.

Commercial Manganese Silicides. PAUL LEBEAU (*Bull. Soc. chim.*, 1903, [iii], 29, 797—798).—A specimen of a commercial silico-manganese, which was brittle, had an irregular, sparkling fracture, and when polished resembled steel, was found to be readily attacked by nitric acid, which left undissolved a quantity of powder consisting of (a) prismatic crystals, resembling those of the manganese silicide, Mn_2Si , and (b) irregular grains, having the average composition, manganese, 71.36; silicon, 22.81; carbon silicide, 2.24; iron, 2.51 per cent., with traces of calcium, and consisting probably of a eutectic mixture of the silicides MnSi and Mn_2Si .

A specimen of manganese, prepared by Goldschmidt's process and containing 5.25 per cent. of silicon, was found to be completely soluble in dilute nitric acid. This, in the author's opinion, does not indicate the absence of the silicide, Mn_2Si , but rather that, owing to the solubility of this in the excess of molten manganese, a homogeneous solid is produced on cooling in which the silicide is in a finely-divided state, and is carried into solution together with the excess of manganese when treated with nitric acid.

T. A. H.

Colloidal Zirconium. EDGAR WEDEKIND (*Zeit. Elektrochem.*, 1903, 9, 630).—A mixture of magnesium and zirconia is heated over an ordinary blowpipe in a metallic crucible. Zirconium (or possibly an alloy of zirconium and magnesium) is formed, and when extracted with hydrochloric acid and washed with water a portion of the zirconium passes into solution in the colloidal condition. The solution is blue by transmitted, turbid by reflected, light. It is coagulated by electrolytes with difficulty or not at all, whilst hydrogen peroxide precipitates it without itself being decomposed.

T. E.

Binary Uranium Compounds. A. COLANI (*Compt. rend.*, 1903, 137, 382—384).—The author has prepared a series of binary compounds of uranium with non-metallic elements by passing dry hydrogen mixed

with the vapour of the appropriate element or the hydride of the element over the double chloride of sodium and uranium, maintained at temperatures between the melting and boiling points of this salt.

Uranium selenide, USe , is crystalline and inflames spontaneously when prepared at a low temperature. The selenide of the formula U_4Se_3 is produced at 1000° in presence of a rapid current of hydrogen carrying small quantities of selenium vapour.

Uranium telluride, U_4Te_3 , is produced in small quantities by the general method, but is best obtained by fusing the double chloride with sodium telluride; it crystallises in square tablets and is black with a metallic lustre.

Uranium phosphide, U_3P_2 , best obtained by fusing sodium uranium chloride with aluminium phosphide, is a black, crystalline powder. The *arsenide*, U_3As_2 , and the *antimonide*, U_3Sb_2 , resemble the phosphide. Uranium nitride and sulphide have also been prepared by the general method.

These compounds burn with difficulty in air, but produce vivid sparks when projected into the Bunsen flame: they are violently attacked by nitric acid.

T. A. H.

Crystalline Bismuth Salts. AUGUST DE SCHULTEN (*Bull. Soc. chim.*, 1903, [iii], 29, 720—724. Compare *Abstr.*, 1900, ii, 353).—The salt, $5\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, obtained by dissolving 50 grams of bismuth nitrate in 50 c.c. of nitric acid of sp. gr. 1.2, and carefully diluting with 3 litres of water, crystallises in thin, hexagonal plates and has a sp. gr. 4.928 at 15° ; on further diluting the mother liquors from this salt, the compound $5\text{Bi}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ slowly separates in monoclinic plates having a sp. gr. 5.290 at 15° .

Bismuth phosphate, BiPO_4 , is obtained in microscopic crystals by adding water very slowly to a solution of bismuth nitrate and sodium phosphate in concentrated nitric acid; it has a sp. gr. 6.323 at 15° .

Bismuth arsenate, BiAsO_4 , obtained similarly, forms monoclinic prisms and has a sp. gr. 7.142 at 15° .

W. A. D.

Preparation of Argon by means of Electric Sparks. AUGUST BECKER (*Zeit. Elektrochem.*, 1900, 9, 600—602).—The quantity of nitrogen oxides formed when air is sparked is approximately proportional to the length of the spark; the length of spark is limited in practice by the difficulty of insulating the electrodes when a high *E.M.F.* is used. The air should also pass the spark at such a rate that it is completely acted on whilst at the same time the oxides of nitrogen produced are not again decomposed. These conditions are fulfilled by passing the air through a brass tube (5 cm. diameter) contracted in the centre by a brass disc with a central hole which forms one electrode, the other electrode consisting of a copper wire insulated by a glass tube. The spark is 1.8 cm. long. With a mixture of equal volumes of air and oxygen, each sparking tube gives an absorption of about 4 litres per hour.

T. E.

Atomic Weight of Radium. W. MARSHALL WATTS (*Phil. Mag.*, 1903, [vi], 6, 64—66).—Relationships similar to those previously described (this vol., ii, 253) appear to exist between the spectra of radium, mercury, barium, and calcium, and from these the author attempts to calculate the atomic weight of radium. The values so obtained vary between 220·3 and 227·3, and the mean of 11 values is 224·89, agreeing closely with that experimentally obtained by Madame Curie, namely, 225.

L. M. J.

Mineralogical Chemistry.

Tellurides at Kalgoorlie. E. H. LIVEING (*Eng. and Mining J.*, *New York*, 1903, 75, 814. Compare this vol., ii, 378).—The following tellurides are recognised as occurring at Kalgoorlie, Western Australia. Calaverite; the extreme results of the assay of many samples are given under I and II. A "specular" telluride, to which the name *speculite* is given, from the Lake View Consols, is nearly white with a bismuth-like tinge of colour, and a perfect cleavage like sylvanite, which it closely resembles except in sp. gr. (8·64) and composition (anal. III and IV). Sylvanite is silver-white and has a perfect cleavage; sp. gr. 8·05 (anal. V and VI). Between the last two are varieties (VII and VIII) which are probably mixtures; some are devoid of cleavage. Petzite is dark steel-grey and has no cleavage (anal. IX and X). The variations in the analyses of "kalgoorlite" indicate that this is a mixture of petzite and coloradoite.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Au.	42·0	40·6	36·6	36·1	25·5	26·1	33·4	29·2	25·15	25·3
Ag.	0·8	2·2	3·50	4·45	11·2	11·4	6·0	10·6	40·95	41·20

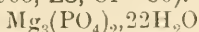
L. J. S.

Apatite from Rhenish Prussia. A. SACHS (*Centr. Min.*, 1903, 420—421).—Massive and crystallised apatite of a pale red colour occurs with quartz and chalcopyrite in the Prinzenstein mine near St. Goar. The high value of the angle $\alpha(0001:10\bar{1}1) = 40^{\circ}21'$ would indicate the presence of only a small amount of chlorine, which is in agreement with the following analysis:

CaO.	MgO.	Al ₂ O ₃ .	FeO.	MnO.	K ₂ O.	Na ₂ O.
54·08	0·04	0·25	0·02	0·01	0·17	0·13
P ₂ O ₅ .	F.	Cl.	SiO ₂ .	H ₂ O.	Total.	Sp. gr.
42·93	2·19	0·02	0·03	0·24	100·11	3·14

L. J. S.

Crystallised Magnesium Phosphate and Arsenate: Artificial Production of Bobierite and Höernesite. AUGUST DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 81—86).—Crystals of



(sp. gr. 1·640) are deposited from mixed solutions at 10° of $\text{MgSO}_4, 7\text{H}_2\text{O}$ (20 grams in two litres) and of $\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$ and NaHCO_3 (19·4 and 4·5 grams respectively in 1 litre). With more concentrated solutions, the precipitate is amorphous. At 20—25° in a more dilute solution, crystals of $\text{Mg}_3(\text{PO}_4)_2, 8\text{H}_2\text{O}$ (bobierite) are formed. Larger monoclinic crystals of bobierite (sp. gr. 2·195) were obtained by the method employed for the artificial production of monetite (*Abstr.*, 1902, ii, 89).

Crystallised $\text{Mg}_3(\text{AsO}_4)_2, 22\text{H}_2\text{O}$ (sp. gr. 1·788) and $\text{Mg}_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$ (höernesite, sp. gr. 2·609) were prepared by similar means; and between temperatures of 0° and 100° no magnesium arsenates other than those with $8\text{H}_2\text{O}$ and $22\text{H}_2\text{O}$ were obtained.

Crystallographic determinations of the artificial bobierite and höernesite are given.

L. J. S.

Artificial Production of Erythrite, Annabergite and Cabrerite. AUGUST DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 87—90).—Crystals of erythrite, $\text{Co}_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$, are obtained by allowing a solution of $\text{Na}_2\text{HAsO}_4, 7\text{H}_2\text{O}$ (2 grams in a litre) to drop slowly into a solution of CoSO_4 (2 grams in 3 litres) heated on a water-bath. Crystallised annabergite, $\text{Ni}_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$, was obtained, but with more difficulty, by the same method. Crystals of cabrerite, $(\text{Ni}, \text{Mg})_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$, were also obtained.

All three substances crystallise in the monoclinic system, and have sp. gr. 3·178, 3·300 and 2·288 respectively (compare this vol., ii, 647).

L. J. S.

Artificial Production of Köttigite and Adamite. AUGUST DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 91—94).—The amorphous precipitate obtained by mixing a solution of $\text{ZnSO}_4, 7\text{H}_2\text{O}$ (4·5 grams in 2 litres) with one of $\text{Na}_2\text{HAsO}_4, 7\text{H}_2\text{O}$ (3 grams in 1 litre), when allowed to remain in contact with the liquid, changes in the course of 8 days to small crystals of köttigite, $\text{Zn}_3(\text{AsO}_4)_2, 8\text{H}_2\text{O}$ (sp. gr. 3·309). Crystals with part of the zinc replaced by cobalt, as in the natural mineral, were also obtained.

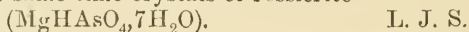
If the crystalline deposit of köttigite be heated with the mother-liquor on a water-bath, it is transformed into small crystals of adamite, $\text{Zn}_3(\text{AsO}_4)_2, \text{Zn}(\text{OH})_2$. Purer orthorhombic crystals of adamite (sp. gr. 4·475) were obtained by allowing a solution of $\text{Na}_2\text{HAsO}_4, 7\text{H}_2\text{O}$ (3 grams in 1 litre) to drop slowly into a hot solution of $\text{ZnSO}_4, 7\text{H}_2\text{O}$ (4·5 grams in 2 litres).

L. J. S.

Simultaneous Production of Struvite and Newberyite and of Arsenical Struvite and Rösslerite. AUGUST DE SCHULTEN (*Bull. Soc. franç. Min.*, 1903, 26, 95—98).—Crystals of struvite (sp. gr. 1·711) are obtained by mixing two solutions, one containing 20 grams of $(\text{NH}_4)_2\text{HPO}_4$, 10 grams of $(\text{NH}_4)_2\text{SO}_4$, and 12 grams of phosphoric

acid of sp. gr. 1.555 in 80 c.c., and the other 16 grams of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 120 c.c. When allowed to remain in contact with the liquid, crystals of newberyite are developed at the expense of the struvite.

In a similar manner, fine orthorhombic crystals (sp. gr. 1.932) of the arsenic compound, $(\text{NH}_4)\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, isomorphous with struvite were obtained, and at the same time crystals of rösslerite



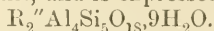
Potash-soda-mica as a Druse-mineral at Striegau. A. SACHS (*Centr. Min.*, 1903, 422—423).—A finely scaly green mineral with pearly lustre occurring on albite in drusy cavities in the Striegau granite gave the following results on analysis, proving it to be similar to the margarodite variety of muscovite:

SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO
45.93	30.95	2.83	0.07	1.15	0.34
K_2O	Na_2O	Li_2O	H_2O	Total.	
9.22	6.04	0.09	3.70	100.32	

Other kinds of mica (biotite, phlogopite, lepidolite, and zinnwaldite) have been noted as secondary minerals in the druses of the Striegau granite, but muscovite only rarely. L. J. S.

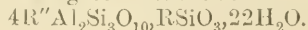
Zeolites from the Neighbourhood of Rome. FERRUCCIO ZAMBONINI (*Jahrb. Min.*, 1902, ii, 63—96).—A description is given of the zeolites (phillipsite, gismondite and chabazite) which occur in cavities in the leucites near Rome. Phillipsite is found as twinned crystals (anal. II—IV) and as radially fibrous spheres (anal. I); the composition is not constant, and with decrease in silica there is an increase in lime and a decrease in potash. This suggests a mixture of two silicates, $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, but this does not hold good for phillipsite from other localities.

In the leucitite of Casal Brunori and Mostacciano, the most abundant zeolite is one which agrees with phillipsite in form, but contains less silica (anal. V—VIII) than typical phillipsite; for this zeolite, the name *pseudophillipsite* is proposed. The crystals consist of eight individuals twinned together, and are pseudo-octahedral in habit, resembling gismondite in general appearance. Radially fibrous spheres also occur, as shown by analysis VI (the other analyses being of crystals). Whilst phillipsite shows variations in composition, that of pseudophillipsite is constant, and is expressed by the formula



The structure of the pseudo-octahedral twinned forms of gismondite is described; analyses (IX—XI) of crystals from three localities all agree with the new formula $\text{R}''\text{Al}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$, which is identical with the hypothetical formula of one of the end members of Streng's chabazite series.

Chabazite in twinned crystals of the phacolite habit gave analysis XII, and spheres of the same mineral gave XIII; these contain less silica than usual, and agree with the formula



The amount of water given off by each of the above zeolites at different temperatures is stated, and the difference between phillipsite and pseudophillipsite in this respect is represented by curves.

	Phillipsite.				Pseudophillipsite.				Gismondite.			Chabazite.	
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.*	X.	XI.	XII.	XIII.
SiO ₂ .	41.37	43.79	40.01	39.34	37.79	38.02	38.21	37.84	33.45	33.6	33.48	40.51	41.32
Al ₂ O ₃ .	23.15	23.77	25.98	25.82	25.55	24.98	25.69	24.19	28.38	27.92	28.21	20.99	21.69
CaO.	8.03	5.28	9.16	9.44	11.84	11.15	10.08	10.98	14.54	14.41	14.76	10.27	9.34
K ₂ O.	9.38	10.93	7.49	7.43	4.16	3.54	6.82	4.63	2.44	2.33	2.23	6.52	6.16
H ₂ O.	17.73	16.04	17.46	17.81	20.60	22.01	19.45	19.84	20.92	20.97	21.69	20.98	21.63
	99.66	99.81	100.10	99.84	99.91	99.70	100.25	99.48	99.90	99.40	99.77	99.27	100.35

* Fe₂O₃, 0.17.

L. J. S.

Chrysocolla: a Remarkable Case of Hydration. CHARLES M. PALMER (*Amer. J. Sci.*, 1903, [iv], 16, 45—48).—As shown by the following analyses, chrysocolla loses an unusually large proportion of its water over sulphuric acid, this loss being unaccompanied by any change in the appearance of the material. On exposure to moist air, slightly more than this amount of water is again absorbed. The loss at 100° is only slightly greater than that over sulphuric acid. Some of this hygroscopic water must have been neglected in previously published analyses of chrysocolla. Analysis I is of impure blue material from Pinal Co., Arizona; II, of blue material from Arizona, and III, of green material from Pinal Co.

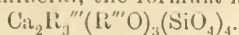
	SiO ₂ .	CuO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	H ₂ O. (over H ₂ SO ₄).	H ₂ O (at low red heat).	Total.
I.	38.64	25.22	11.76	trace	—	—	—	12.36	12.22	100.20
II.	35.84	31.50	3.74	„	trace	1.76	0.16	18.96	8.32	100.28
III.	33.28	30.76	4.60	„	„	not detd.	not detd.	20.54	8.60	97.78

L. J. S.

Hellandite, a New Mineral. WALDEMAR C. BRÖGGER (*Nyt Mag. Naturvid. Kristiania*, 1903, 41, 213—221).—Dull crystals of this new mineral occur with sphene, tourmaline, apatite, and thorite in the pegmatite-veins near Kragerö, Norway. They are prismatic in habit, but belong to the monoclinic system; $a:b:c=2.0646:1:2.1507$; $\beta=70^\circ 15'$. Most crystals are altered to a yellow or white, earthy material; a few are leather-yellow to brownish-black. The least altered and blackest material is the hardest (II about 5); sp. gr. 3.55; it has a conchoidal fracture, and a greasy to resinous lustre, and is optically isotropic and amorphous (like gadolinite, orthite, &c.); analysis, by O. N. Heidenreich, gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Mn ₂ O ₃ .	(Ce, Di, La) ₂ O ₃ .	CaO.
23.55	10.22	2.64	5.69	40.12	10.05
MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.	
0.05	0.26	0.06	7.55	100.19	

The mineral is readily soluble in hydrochloric acid with evolution of chlorine. Neglecting the water, the presence of which is probably due to the alteration of the mineral, the formula is deduced as



Both in crystalline form and chemical composition, hellandite is analo-

gous to guarinite (Abstr., 1896, ii, 309), and, to a certain extent, is also related to the datolite-homilite-gadolinite group. L. J. S.

Plumasite, an Oligoclase-corundum-rock from California. ANDREW C. LAWSON (*Bull. Dep. Geol. Univ. California*, 1903, 3, 219—229).—Only since the experiments of Morozewicz (Abstr., 1899, ii, 762) has corundum been recognised as an essential constituent of an igneous rock; since then, corundum-syenites have been described from India, the Urals, Ontario, and Montana. The corundiferous igneous rock now described occurs as a dyke in amphibole-peridotite, near Spanish Peak, in Plumas County. It is composed of coarse, granular, white oligoclase (analysis, by J. Newfield, below), with embedded crystals (acute rhombohedra) of pale violet-blue corundum, the two minerals being present in the proportion of 84 to 16 respectively:

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O.	Total.	Sp. gr.
61.36	22.97	5.38	8.08	1.72	99.51	2.633

L. J. S.

Boogaldi, Barratta, Gilgoi, and Eli Elwah Meteorites, New South Wales. ARCHIBALD LIVERSIDGE (*J. and Proc. Roy. Soc. New South Wales*, 1902, 36, 341—359, plates III—XV).—*Boogaldi*.—This iron, weighing 2057.5 grams, was found in 1900 at a spot about 2 miles from the Boogaldi post-office. It is roughly pear-shaped, without pittings, and shows on the surface well-marked lines of flow. The structure is octahedral; sp. gr. 7.85. The results of a partial analysis are given under I. Some minute yellow and white metallic spangles, which were insoluble in nitric acid, and therefore presumably gold and a metal of the platinum group, were isolated from this meteorite.

Barratta.—The first stone of this fall was found about 1860, and two more masses were found later; of the latter, No. 2 weighs 31½ lbs., and has sp. gr. 3.706, and No. 3, 48 lbs., sp. gr. 3.429. The non-metallic portion of No. 2 gave, on analysis, the results under II*b*, and the metallic portion (amounting to 6.13 per cent. of the whole) those under II*a*.

Gilgoi.—This stone, of 67½ lbs. and sp. gr. 3.857, was found at Gilgoi Station, in 1889. It contains 14.7 per cent. of magnetic material (analysis III*a*); the non-magnetic portion gave III*b*. Gold is probably present in this meteorite. A second mass of 74¼ lbs., sp. gr. 3.757, was found at the same locality.

Eli Elwah (or *Hay*).—This was found before 1888 at Eli Elwah, 15 miles west of Hay; it weighed 33½ lbs. and has sp. gr. 3.537. Analysis IV:

	Fe.	Ni.	Co.	Cu.	As.	Cr.	Mn.	C.	S.	P.	Insol. in HCl.	Total		
I.	91.14	8.05	0.48	0.28	trace	n. d.	—	n. d.	n. d.	n. d.	0.04	99.99		
IIa.	81.11	8.53	0.12	—	—	—	nil	—	n. d.	n. d.	1.86	—		
IIIa.	82.46	8.35		—	—	—	—	—	trace.	nil.	1.51	—		
	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	Mn.	Ni.	Co.	CaO.	MgO.	Na ₂ O.	K ₂ O.	S.	P.	Total.
IIb.	41.67	1.16	10.10	15.66	trace	0.48	nil	2.71	25.82	0.61	0.09	2.06	0.07	100.43
IIIb.	42.69	4.98	6.70	12.67	trace	0.28	nil	17.53	12.66	0.74	0.10	2.54	0.14	101.03
IV.*	39.47	2.87	9.17	17.06	trace	1.01	nil	1.61	25.58	0.74	0.11	2.30	0.10	100.02

* Cl, trace; Cu, Sn, Cr, V, absent.

L. J. S.

Physiological Chemistry.

Replacement of Inorganic Constituents of the Organism by Others. THOMAS BOKORNY (*Pflüger's Archiv*, 1903, 97, 134—147).—The similarity of potassium to rubidium and caesium, and of calcium to barium and strontium, suggested experiments to ascertain whether one element can replace another in the organism without harm. The present experiments on the cultivation of moulds in different media lend no support to the idea that this is possible. W. D. H.

Is Muscle Juice a Result of Autolysis? SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1903, 4, 182—184).—Vogel has stated that it is impossible, even with great pressure, to express a juice from muscle until many hours after death. He thinks, therefore, the formation of juice is due to a post-mortem autolytic change which liquefies the muscle proteids. No confirmation of this result was obtained; the author had no difficulty in obtaining plenty of muscle plasma from perfectly fresh muscles with a simple hand-press, as Kühne, Halliburton, and others have done previously. W. D. H.

Presence of Lactic Acid in the Muscles of Invertebrates and the Lower Vertebrates. JEAN GAUTRELET (*Compt. rend.*, 1903, 137, 417—418).—Muscle of *Scyllium canicula* was macerated with water, and the albumin in the aqueous extract was coagulated by boiling. Addition of lead acetate caused the precipitation of the chlorides, phosphates, and sulphates, and ammoniacal lead acetate was added after filtration. The lead was removed from the filtrate by means of hydrogen sulphide, and the liquid on concentration deposited crystals of creatine. The mother liquor, when acidified with sulphuric acid, yielded *D*-lactic acid on extraction with ether.

In the same way, lactic acid has been identified in the muscle of *Mustelus* (Selachoides) and of *Maia* (Crustacea). In the last, no creatine was found. J. McC.

Refraction Coefficient of Serum Proteids. EMIL REISS (*Beitr. chem. Physiol. Path.*, 1903, 4, 150—154).—The serum proteids were separated by fractional precipitation with ammonium sulphate and examined with Pulfrich's refractometer, the refraction of adherent salt being allowed for. The values of n_D for 1 per cent. of proteid are given as follows:

Euglobulin	0.00230	Crystallised albumin ...	0.00201
Pseudo-globulin—			
First fraction	0.00224	Amorphous albumin ...	0.00183
Second fraction ...	0.00230	Total proteid	0.00172

It cannot be said that this helps in establishing a specific difference between the two globulins. The difference between the globulins and

albumin is quite evident. The last figure is very puzzling and requires further explanation. W. D. H.

Meat Extract. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1903, 39, 126—132).—The author's own experiments lead to the conclusion that the succinic acid obtained from meat extract by Kutscher and Steudel (this vol., ii, 499) was not originally present in the extract, but was produced from nucleone and other substances under the influence of the excess of sulphuric acid employed. J. J. S.

Influence of Putrefaction on the Amount of Succinic Acid in Meat. HEINRICH WOLFF (*Beitr. chem. Physiol. Path.*, 1903, 4, 254—258).—The question of the origin of succinic acid in meat extract has been recently reopened by Kutscher and Steudel. In the present research, it was found that the putrefaction process, especially in its later stages, led to the formation of a large amount of the acid. The origin of this substance in Liebig's extract (whether due to method of preparation or to the use of faulty material) is left open. W. D. H.

Biological Behaviour of Nerol, Geraniol, and cycloGeraniol. HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1903, 4, 251—253).—Nerol and geraniol are intensely toxic as tested on mice; in small doses, no difference in their action can be noted, although on other grounds the two substances are not regarded as identical. *cyclo*-Geraniol is much less toxic; this coincides with the relationship between the aldehyde citral and its corresponding cyclic isomeride. W. D. H.

Estimation of Lipase Activity. CHARLES GARNIER (*Compt. rend. Soc. Biol.*, 1903, 55, 1094—1096).—In order to determine the power of a lipase, it is necessary to take the mean of several parallel estimations with the same solution. Reasons are given why the method adopted by Hanriot, of taking the average of estimations following one another with the same mixture of ferment and monobutyryl after neutralising the acid formed in each experiment, gives incorrect results. The butyrate formed and the quantity of monobutyryl left are important factors. W. D. H.

Action of Pancreatic Lipase in the Presence of Blood. MAURICE DOYON and ALBERT MOREL (*Compt. rend. Soc. Biol.*, 1903, 55, 984—985).—No diminution of the ethereal extract of the blood occurs if the latter is incubated in a vacuum. Hanriot holds that this is because under these conditions lipase is unable to act, but it is now shown that pancreatic lipase in the presence of blood acts as well on fats in a vacuum as in contact with air. Defibrinated blood or serum splits monobutyryl, tributyrin and other ethers as well in a vacuum as in contact with air. W. D. H.

Glycerol in the Blood. MAURICE NICLOUX (*Compt. rend.*, 1903, 137, 70—73).—Glycerol injected into the blood disappears with great rapidity, being eliminated readily by the kidneys. W. D. H.

Glycerol in the Blood. MAURICE DOYON and ALBERT MOREL (*Compt. rend. Soc. Biol.*, 1903, 55, 983—984).—Contrary to Hanriot's assertion, the diminution of the ethereal extract which occurs when blood is preserved aseptically in an incubator is not due to saponification. The amount of glycerol estimated by Nicloux's method does not increase.

W. D. H.

Antiferments. ARISTIDES KANITZ (*Zeit. Biol.*, 1903, 45, 117—118). ERNST WEINLAND (*ibid.*, 119—120).—Weinland has stated that the increase of acid beyond 0.2 per cent. hydrochloric acid lessens and finally annuls the action of antitrypsin, but that increase of alkalinity from 0.4 to 1 per cent. of sodium carbonate has little or no influence. The first paper points out that the amount of sodium hydroxide liberated is not proportional to the amount of sodium carbonate, but to its square root. The difference between a 0.4 and a 1 per cent. solution is therefore very small, and insufficient to argue from. To this, Weinland replies that the differences are those which fall within physiological limits; what the effect of higher alkalinities may be is a matter of physiological indifference. The differences of alkalinity observed have a distinct influence on other ferments and ferment-like substances. The effect of high alkalinity on antitrypsin cannot be accurately gauged, as increase of alkali affects trypsin injuriously (Vernon).

W. D. H.

Nature of Fibrin-ferment. CORNELIS A. PEKELHARING and WILLEM HUISKAMP (*Zeit. physiol. Chem.*, 1903, 39, 22—30).—The authors have previously stated that various nucleo-proteids can, after union with calcium, play the part of the fibrin-ferment. Hanumarsten regards it as doubtful whether different materials can act in this way, but thinks it more probable that the effect is due to traces of a single proteid (prothrombin) adhering to the various preparations. In the present paper, the authors reaffirm with fresh experiments their original contention.

W. D. H.

Physiological Action of the Proteoses. FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1903, 9, 343—373).—The well-known physiological effects of proteoses have been attributed by Pick and Spiro to impurities mixed with them. In the present research, no valid grounds were found for this supposition. There are, no doubt, differences in the response of different animals, depending largely on factors in which immunity plays a part, but proteoses prepared in various ways, and subjected to rigorous purification, were found in all cases to cause typical physiological effects.

W. D. H.

Enzyme of the Blood which Causes Decomposition of Hydrogen Peroxide. I. GEORGE SENTER (*Zeit. physikal. Chem.*, 1903, 44, 257—318).—When defibrinated blood is treated according to Bergengrün's method, the substance that is catalytically active in the decomposition of hydrogen peroxide is found to have gone almost completely into the filtrate along with the hæmoglobin, and may, along with the

latter, be passed through a Berkefeld filter without any noticeable loss of catalytic efficiency. The catalytically active substance in this solution may be separated from the hæmoglobin (which does not itself appreciably affect hydrogen peroxide) by precipitation with 50 per cent. alcohol. If the reddish-brown precipitate thus obtained is freed from alcohol and dissolved in water, a transparent, pale yellow solution is formed, which is shown to be free from hæmoglobin by spectroscopic examination, and which possesses strong catalytic power. For the enzyme thus isolated, the name "hæmase" is suggested. Guaiacum tincture containing hydrogen peroxide is not turned blue, nor is indigo in sulphuric acid solution (also containing hydrogen peroxide) bleached, by a solution of hæmase.

In order to study quantitatively the influence of hæmase on the decomposition of hydrogen peroxide, it was found advisable to work at 0°, for at higher temperatures the oxidation of the enzyme by the peroxide begins to be appreciable.

The course of decomposition of hydrogen peroxide in dilute solution (1/300—1/1100 molar), as determined by titrating samples of the reaction mixture with potassium permanganate, is exactly that required by the law of mass action, according to the equation

$$-dC_1/dt = kC_1C_2,$$

where C_1 and C_2 are the concentrations of the peroxide and the enzyme respectively. When the hydrogen peroxide solutions are more concentrated, there are slight deviations from the simple law. At 10°, the velocity coefficient is 1.5 times greater than at 0°.

In presence of hydrochloric, nitric, or acetic acid, the catalytic decomposition is markedly retarded, but the enzyme is not permanently affected, and recovers on neutralisation of the acid. This "poisoning" effect is stronger for nitric acid than for hydrochloric acid, and is in both cases nearly proportional to the cube of the concentration. Addition of sodium hydroxide also retards the catalytic decomposition, but in this case also the enzyme is not permanently affected. Potassium nitrate and chlorate in very small quantities exert a marked retarding influence on the decomposition. Furthermore, as regards this enzyme, aniline is to be regarded as a weak, and hydrogen cyanide as a very strong, "poison."

A solution of hæmase loses its catalytic efficiency if it is kept at 40—60° for a short time; the rate at which the enzyme becomes inefficient increases rapidly with the temperature to which it has been raised, and is, for example, 6—7 times greater at 55° than at 45°. Moreover, this rate is especially great during the first portion of the period of exposure to the high temperature.

Emphasis is laid on the analogy between the action of enzymes and of inorganic catalytic agents. The inorganic agent specially considered is colloidal platinum, studied by Bredig and his pupils (Abstr., 1900, ii, 213; 1901, ii, 441). In comparing the influence of hæmase and of colloidal platinum on the decomposition of hydrogen peroxide, it is noted that in both cases the temperature coefficient of the velocity constant is small (1.5 and 1.7 respectively, for an interval of 10°). Further, the retarding effect of certain "poisons" is very similar in the two cases. On the other hand, the efficiency of hæmase is easily

destroyed by rise of temperature, but that of colloidal platinum is less affected.
J. C. P.

The Blood Proteids in a Case of Alkaptonuria. EMIL ABDERHALDEN and W. FALTA (*Zeit. physiol. Chem.*, 1903, 39, 143—146).—In alkaptonuria, homogentisic acid occurs in the blood-serum. The blood proteids contain tyrosine and phenylalanine in about the same proportions as in normal cases. The cause of the condition is not to be sought in the digestive or absorptive processes, but is due to a localised, specific breakdown of the proteid molecule. W. D. H.

Action of Ricin on Fishes' Blood. ALBERT FRAENKEL (*Beitr. chem. Physiol. Path.*, 1903, 4, 224—233).—The observations were made with the blood of *Barbus fluviatilis*; this blood shows a certain amount of natural immunity towards ricin, and is not agglutinated so much as the blood of mammals. This depends not on the amount of receptor groups in the corpuscles, but is due in great measure to the presence of a strong ricin anti-agglutinin in the serum. Hemolysis is nearly related to agglutination. W. D. H.

Nature and Determination of the Alkalinity of the Blood. HENRI LABBÉ (*Compt. rend.*, 1903, 137, 384—385).—The total alkalinity of the serum is first determined by titration with centinormal sulphuric acid; the phosphates are then precipitated with barium chloride, and titration again performed with acid; the difference is the "apparent alkalinity" due to mineral phosphates. Some importance is attributed to ptomaines and leucomaines in producing the total alkalinity, and the suggestion is made that light will be thrown on disease by the examination of the alkalinity of the blood in pathological cases. W. D. H.

Precipitins. A. HUNTER (*Proc. Physiol. Soc.*, 1903, ix; *J. Physiol.*, 30).—Rabbits were treated with 5 to 7 injections of the separated proteids (albumin, euglobulin, pseudo-globulin) of ox-serum. In each case, precipitins were obtained. In some cases, precipitins were obtained after one injection only; they are always appreciable after the 3rd and abundant after the 5th injection. If a fresh injection is performed on a rabbit, the blood of which is already rich in precipitin, there is an immediate diminution and usually a complete disappearance of the precipitin; this gradually reappears about the second or third day, and attains a maximum which is higher than the previous maximum about the fifth or sixth day. The polymorphonuclear leucocytes follow quantitatively a course exactly inverse to that of the precipitins. W. D. H.

Heart Action of *Molgula Manhattensis*. GEORGE WILLIAM HUNTER, jun. (*Amer. J. Physiol.*, 1903, 10, 1—27).—The main purport of the paper is to show that the peristalsis of the heart of this ascidian is under the control of the central nervous system. Part of the evidence relates to drug action. In some cases (alcohol, muscarine, nicotine, strychnine), the heart of normal *Molgula* reacted in a different

manner from those in which the ganglion (brain) had been removed. In other cases, in which the drugs employed (caffeine, digitalin) were muscle poisons rather than nerve poisons, removal of the ganglion made no difference.

W. D. H.

Chemistry of Lymphatic Organs. I. IVAR BANG (*Beitr. chem. Physiol. Path.* 1903, 4, 115—138).—The present communication relates to the nucleo-proteid and nucleo-histon obtainable from the thymus gland. Analyses are given, and discrepancies between these and those given by Huiskamp and others pointed out. Among the important analytical facts noted, it is shown that dilute acetic acid should not be employed in the precipitation of such substances; it is not an indifferent reagent, but splits the nuclein compound into two parts, one of which is easily soluble whilst the other subsequently dissolves with difficulty in dilute alkali. The former appears to be an acid albuminate. More dependence is placed on the methods of salt and alcohol precipitation.

W. D. H.

Extirpation of the Thymus. SWALE VINCENT (*Proc. Physiol. Soc.*, 1903, xvi; *J. Physiol.*, 30). **Physiological Effects of Thymus Extracts** (*ibid.*, xvii).—Removal of the thymus in frogs and guinea-pigs produces no appreciable effects. Subcutaneous injection of extracts made with boiling saline solution in frogs or mammals produces only a slight temporary stimulant effect. Intravenous injection causes a fall of blood pressure, which is lessened but not abolished by atropine or section of the vagi. There is no evidence of any specific action of these extracts, and the effects are comparable with those obtained by the injection of extracts of almost every tissue of the body, although whether the depressor substances are identical in the different tissues cannot yet be affirmed.

W. D. H.

Digestion and Absorption in the Stomach. FELIX REACH (*Beitr. chem. Physiol. Path.*, 1903, 4, 139—144. Compare Abstr., 1901, ii, 667).—Dogs' stomachs in a state of full digestion of a meat meal were removed, placed in a chamber at body temperature, and their contents examined 4 hours later. After removal of the still coagulable proteids, albumose nitrogen was estimated in the precipitate produced by saturation with zinc sulphate, and peptone nitrogen in the precipitate produced by adding picric acid to the filtrate; these two quantities were subtracted from the total nitrogen, and the difference gives that of the end products (peptoids, complex substances which give no biuret reaction, and crystalline materials). The following table gives the results of the four experiments:

Amount of flesh given.	Albumoses.	Percentage of nitrogen in	
		Peptone.	End-products.
100	56.4	43.6	
200	48.7	19.9	31.4
300	32.2	35.0	32.8
400	37.9	30.1	32.0

In digestion *intra vitam*, Zunz gives the percentage of albumose nitrogen as 90, which is much higher than in the present experiments. In these, however, the conditions excluded any absorption. In Zunz's experiments, no doubt the simpler and more diffusible products were rapidly absorbed, and this will account for the large amount of albumoses.

It is further pointed out that in artificial digestions pepsin is employed. In natural digestion, Glaessner's pseudo-pepsin, if it really exists, is in action also. This may account for some of the differences observed in digestion experiments carried out *in vitro* and *in vivo* respectively.

W. D. H.

Action of Glycerol Extracts of Gastric Mucous Membrane on Monobutyrim. ELOPHE BÉNECH and L. GUYOT (*Compt. rend. Soc. Biol.*, 1903, 55, 994—996).—Glycerol extracts of the mucous membrane of the horse's stomach contains a lipase which decomposes monobutyrim. That from the cardiac region is about twice as energetic as that from the pyloric region; the action is most marked at 40°, and is destroyed at 70°; the amount of fat decomposed does not increase proportionally with lapse of time, but tends to reach a limit. The extracts are sensitive to the action of alkali, but not so much so to that of hydrochloric acid. Within certain limits, the enzyme obeys Schütz's law. Enterokinase does not appear to favour its action.

W. D. H.

Influence of Tryptic Digestion on Precipitin Reactions. KARL OPPENHEIMER (*Beitr. chem. Physiol. Path.*, 1903, 4, 259—261).—The question whether the precipitating substance and the substance precipitated in the precipitin reaction are proteids or proteid-like substances, or whether they are only mechanically mixed with the proteids, can be solved, at any rate partially, by determining whether these materials can be affected by proteolytic agents. Previous experiments by the author with Michaelis showed that these substances are affected by pepsin-hydrochloric acid. The present experiments relate to tryptic action. It is shown by experiments on rabbits that the injection of egg-white, thoroughly digested by trypsin, does not produce the appearance of a precipitin in the blood; that a strong anti-egg-white serum has no effect on a pancreatic digest of egg-white, and, finally, that the precipitin action of this serum can be annihilated by tryptic digestion. Egg-white in these particulars differs in no way from blood serum. The opposite results of Obermayer and Pick are attributed to the incomplete action of the trypsin used.

W. D. H.

Change of Cystin into Taurine in the Animal Organism. G. VON BERGMANN (*Beitr. chem. Physiol. Path.*, 1903, 4, 192—211).—The experiments were made on dogs with a biliary fistula. The addition of cystin to the ordinary diet does not appreciably increase the amount of taurine in the bile. The administration of sodium cholate is followed by an increased formation of taurocholic acid to as much as double the normal amount; the excretion persists for 24 hours. After such a procedure, which apparently clears out the accumulated

taurine, the administration of cystin leads once more to an increased excretion of taurine; this is considered to prove that cystin is transformed into taurine in the body. The normal taurine in the bile is believed to originate from the proteid ingested, recent research having shown that part of the proteid sulphur is present there in the form of the cystin group.

W. D. H.

Degradation of Peptides in the Organism. EMIL ABDERHALDEN and PETER BERGELL (*Zeit. physiol. Chem.*, 1903, 39, 9—11).—The isolation of amino-acids by means of naphthalene- β -sulphonic chloride in urine is found to give excellent results so long as not less than 0.25 per cent. of acid is present. Glycine, *i*-alanine, leucine, or phenylalanine injected in doses up to 5 grams are completely consumed in the system of the guinea-pig; glycylglycine, however, is converted into glycine, part of which appears in the urine.

E. F. A.

Digestion of Proteids by the Pancreas Ferments. EMIL FISCHER and EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1903, 39, 81—94).—The cyclic amino-acid, α -pyrrolidinecarboxylic acid, which is formed by the hydrolysis of proteids both with boiling acids and alkalis, has been assumed to be a primary decomposition product. The digestion of casein with pancreas enzyme yields, however, whatever conditions are employed, no trace either of α -pyrrolidinecarboxylic acid or phenylalanine; but, on the other hand, a polypeptide is formed, which resists further action of the enzyme, and on heating with mineral acids yields these two acids in the same quantity as the equivalent amount of casein.

This polypeptide contains also the other amino-acids (leucine, alanine, glutamic, and aspartic acids) normally yielded by casein. It is easily precipitated by phosphotungstic acid, and thus separated without difficulty from the monoamino-acids. Purified by repeated precipitation, it shows no biuret reaction. Exactly similar products are formed in the tryptic digestion of edestine, haemoglobin, egg-albumin, fibrin, and serum-globulin.

E. F. A.

The Metabolic Value of Salt. C. M. BELL (*Zeit. Biol.*, 1903, 45, 182—222).—A very thorough series of observations on man showing the importance of salts, especially of common salt in diet. Absence or paucity of salt does not modify digestion or assimilation, nor does it affect the metabolism of fat or carbohydrate. The loss of body weight observed is due to interference with proteid metabolism, the organ-proteid undergoing increased breakdown. Full references to previous literature are given, and the statement so frequently made by others that salt exercises a sparing influence on proteid is thoroughly confirmed.

W. D. H.

Fatty Acids formed by Ascaris. ERNST WEINLAND (*Zeit. Biol.*, 1903, 45, 113—116).—The fatty acid formed in the life processes of *Ascaris lumbricoides* was formerly stated to be mainly valeric acid (*Abstr.*, 1902, ii, 155). Analysis of the calcium salt shows it to be a mixture of valeric and hexoic acids. In another specimen, pure calcium hexoate was separated out in a crystalline form.

W. D. H.

Synthesis of Fats during Absorption. BENJAMIN MOORE (*Proc. Roy. Soc.*, 1903, 72, 134—151).—In the chyle of the mesenteric lymphatics, the fatty constituents formed in the intestine have been re-synthesised into neutral fat. The epithelial cells, but not those of the mesenteric glands, are concerned in this process. In the mucous membrane, there is still a considerable percentage of free fatty acid, showing that although the synthesis is in progress, it is not complete. The cells of the pancreas, intestinal mucosa, or lymphatic glands, or cell-free extracts of those tissues are unable *in vitro* to affect the synthesis of fat from glycerol and soaps. The living cell *in situ*, supplied as it is with energy from the circulating blood, is able to do this. Theoretical deductions from this are made concerning the cell as an energy transformer, and distinguishing the synthetical power of cells from the transformations (including syntheses) brought about by enzymes. Extracts of pancreas, intestinal mucosa, and mesenteric glands possess the power of liberating free oleic acid from sodium oleate; the alkali split off becomes stably combined with some substance in the extracts and does not recombine with the acid on evaporating down the solutions. The power of setting free oleic acid in this way is lessened, but not destroyed, by boiling the extracts. The change occurs in faintly alkaline solution, and is completed without the reaction becoming acid. No such splitting occurred in control experiments with water or saline solution. Such an alteration, if it occurs in the cells, is probably the initial change which soap undergoes in the synthesis of fat. It is obviously a protective mechanism against the invasion of the body by poisonous soaps. W. D. H.

Human Milk. ADOLF JOLLES (*Zeit. Biol.*, 1903, 45, 248—260).—Human milk contains no oxydases, and as a rule no peroxydases. It, however, decomposes five or six times as much hydrogen peroxide as cow's milk, but there is no proportionality between the amount of catalase and the amount of hydrogen peroxide decomposed. Great value is attached to this reaction. Dilution with water has no influence, but mineral acids and mercury and fluorine compounds have; organic acids have a feeble effect. Neutral salts, bases, and alcohol within certain limits have no influence. Heating to 75° destroys the catalases completely. The constituent of milk which brings about the catalytic action is wholly precipitable by alcohol. W. D. H.

Salol Ferment contained in Certain Milks. ALBERT DESMOULIÈRE (*Compt. rend.*, 1903, 137, 337).—A reply to Miele and Willem (this vol., ii, 604). The author calls attention to the fact that he has already withdrawn his view that the decomposition of salol is effected by a ferment, and explains the action as one of saponification (this vol., ii, 312). J. McC.

Salivary Digestion in the Stomach. W. B. CANNON and H. F. DAY (*Amer. J. Physiol.*, 1903, 9, 396—416).—The experiments given show that salivary digestion can continue in the stomach for a much longer period than is usually considered to be the case. The food lying in the fundus undergoes uninterrupted amylolysis for at least two hours, not

because the proteid protects the ptyalin, but because the absence of peristalsis in this region, until quite late stages in digestion, prevents admixture with gastric juice, especially in the interior of the swallowed masses.

W. D. H.

Proteid Synthesis in the Animal Body. YANDELL HENDERSON and ARTHUR L. DEAN (*Amer. J. Physiol.*, 1903, 9, 386—391).—By feeding a dog on the end-products of proteid decomposition (prepared by the action of a mineral acid on meat), the animal was maintained in nitrogenous equilibrium and did not lose weight. It is quite evident that the nitrogenous substances in the diet were not immediately converted into urea and excreted, but were retained to a considerable extent, and that the portion expended (appearing in the urine) exerted a marked proteid-sparing action. The retention of nitrogen is not in itself a proof of proteid synthesis, and the explanation given of the results is regarded as sufficient without invoking the more radical hypothesis of proteid synthesis.

W. D. H.

Formation of Dextrose from the End-products of Pancreatic Proteolysis. PERCY G. STILES and GRAHAM LUSK (*Amer. J. Physiol.*, 1903, 9, 380—385).—Dogs poisoned with phloridzin were taken as the base level from which the experiments started; they were then fed with the end (crystalline) products of a pancreatic digest, and the increase in the amount of excreted sugar was noted. Dogs do not bear the treatment well, and in only two cases could it be carried through. From these, it appears that for every 5 grams of nitrogen given in this way, 12 of dextrose were excreted. If given in the form of native proteid, 18—19 grams of dextrose would have been expected. The amino-nitrogen given was eliminated quantitatively, and no light is thrown on the question as to whether a proteid synthesis had occurred. The experiments show that it is impossible for a large sugar radicle to exist in the proteid molecule.

W. D. H.

Proteolytic Activities of Pancreatic Juice. WILLIAM M. BAYLISS and ERNEST H. STARLING (*J. Physiol.*, 1903, 30, 61—83).—Fresh pancreatic juice never contains trypsin; it contains trypsinogen and a weak proteolytic ferment, somewhat resembling erepsin; the latter will slowly digest fresh fibrin, or caseinogen, but not coagulated proteid or gelatin. Trypsinogen is a stable substance which is only slowly altered when left in alkaline or acid solutions. Enterokinase is the only reagent found that converts it into trypsin. The view of Pawloff is supported, that the action of enterokinase is like that of a ferment, a small amount of it being able to act on an unlimited amount of trypsinogen provided sufficient time is allowed to elapse. Enterokinase is stable in aqueous solutions at 15°, but is rapidly destroyed at 40°. Trypsin is very unstable, and is rapidly destroyed, especially in alkaline media at the body temperature; this is retarded by the presence of dissolved proteids or peptones. Enterokinase cannot be obtained from blood fibrin, leucocytes, or lymphatic glands as Delezenne has stated. It is a product of the small intestine only, and mainly of its upper end.

Attention is drawn to the high alkalinity of pancreatic juice ; when obtained by the use of secretin injections, 10 c.c. need for its neutralisation from 10 to 15 c.c. of decinormal sulphuric acid. If obtained by the use of pilocarpine injections, the alkalinity is rather less, but it is richer in total solids, especially in proteids ; the proteids are alike qualitatively in both varieties of juice, and all belong to the class of coagulable proteids.

W. D. H.

Digestive Leucocytosis. ALEXANDER GOODALL, G. LOVELL GULLAND, and DIARMID NOËL PATON (*J. Physiol.*, 1903, 30, 1—9).—During digestion, there is a slight preliminary fall in the number of leucocytes ; this is followed by a rise which reaches its maximum four hours after food. The increase affects the lymphocytes (and is in the case of these corpuscles very constant both in incidence and degree), and the polymorphonuclear leucocytes. The eosinophile cells show very little change. No difference could be found between the cells of the mesenteric arteries and veins, and those in the general circulation. Pohl's conclusion that the new cells are produced in the intestinal wall is thus negatived ; there was, moreover, no sign of increased activity in the lymphoid tissue of the intestinal wall. Removal of the spleen makes no difference in the results. The source of the new cells has still to be determined. The experiments were made on dogs and cats.

W. D. H.

Influence of Lecithin on the Growth of the White Rat. SHINKISKI HATAI (*Amer. J. Physiol.*, 1903, 10, 57—66).—The present research confirms previous statements that lecithin is a stimulating agent in normal growth. In the rats which received it either subcutaneously or by feeding, the gain averaged 60 per cent. more as compared with control animals ; they also showed more resistance against unfavourable surroundings. No difference in the nervous system of the two sets of animals was observable.

W. D. H.

Influence of Rennin on Milk Digestion. PHILIP B. HAWK (*Amer. J. Physiol.*, 1903, 10, 37—46).—Statements have recently appeared that the amount of rennin in the stomach of young animals is less than in the adult. The conclusion that rennin is inhibitory to digestion of the milk proteids is confirmed in the present experiments ; this is true for both gastric and pancreatic digestion, and is not due to the mineral constituents of the rennin. Rennin has no inhibitory action on the digestion of egg-albumin.

W. D. H.

Feeding Experiments with Pyrimidine Compounds. II. STEUDEL (*Zeit. physiol. Chem.*, 1903, 39, 136—142. Compare Abstr., 1901, ii, 409).—No sparingly soluble purine derivatives could be found in the urine of a fox-terrier bitch to which ψ -uric acid, isouric acid, or hydrouracil had been administered *per os*. These compounds appear to be completely oxidised in the animal system. Iminomethyluracil (Abstr., 1891, 1007) behaves in a similar manner, whereas methylthiouracil passes through the system unchanged.

J. J. S.

End-products of the Auto-digestion of Yeast and Pancreas.

I. FRIEDRICH KUTSCHER and LOHMANN (*Zeit. physiol. Chem.*, 1903, 39, 159—164).—The present communication relates to the pancreas only. The main interest is the discovery that, in addition to the usual purine and hexon bases, the products of the decomposition of lecithin (choline, glycerophosphoric acid) are present. This suggests a future examination of the behaviour of various digestive juices towards lecithin.

W. D. H.

End-products of Peptic Digestion. LEO LANGSTEIN (*Zeit. physiol. Chem.*, 1903, 39, 208—209).—Some small points of difference between the author's results and those of Salaskin and Kowalewsky (*Abstr.*, this vol., ii, 559) are commented on. It, however, appears certain that amino-acids are obtainable as the result of protracted proteolysis by pepsin.

W. D. H.

Elimination of Sodium Chloride in Normal Fæces and in Diarrhœa. ADOLPHE JAVAL (*Compt. rend. Soc. Biol.*, 1903, 55, 927—928, 928—929).—The amount of sodium chloride in the fæces is normally from 1 to 2 decigrams a day. The addition of 10 grams of salt to the food is followed by its elimination by the urine, the process occupying more than 24 hours. There is simultaneously a slight increase of weight, which is attributed to retention of water. The amount of fæces also increases, the laxative action of salt being well known, but the actual increased amount of salt that leaves the body by this route is very small, and the increase is but temporary. In the diarrhœa of Bright's disease, the amount of salt in the fæces is increased, and in severe cases may be even greater than that in the urine.

W. D. H.

Effect of Diuretics, Nephritic Poisons, and other Agencies on the Urinary Chlorides. TORALD SOLLMANN (*Amer. J. Physiol.*, 1903, 9, 425—453). Comparative Diuretic Effects of Saline Solutions (*ibid.*, 454—465).—A detailed account of experiments previously published in a preliminary communication (this vol., ii, 562).

W. D. H.

Acetone in Normal Horse's Urine. K. KIESEL (*Pflüger's Archiv*, 1903, 97, 480—538).—Acetone is a normal product of metabolism and is always found in the urine of the horse to the extent of a few milligrams per litre. A new method of estimation is given, because Messinger's and other methods which depend on the formation of iodoform cannot be used with horse's urine; the distillate of this urine contains substances other than acetone which unite with iodine. These substances are in part phenol and benzoic acid, but are in great measure not yet identified.

W. D. H.

Indole Formation and Indican Excretion in Rabbits during Inanition. ALEXANDER ELLINGER (*Zeit. physiol. Chem.*, 1903, 39, 44—54).—Blumenthal and Rosenfeld (*Mitt. Würzburger med. Klinik*, 1886, 2, 341) have stated that rabbits in a state of inanition excrete indican, though no indole is present in the

intestinal contents. They attribute the indican to non-bacterial decomposition of proteid in tissue metabolism. If this is the case, the rabbit differs from the dog and cat. By the use of more delicate tests, it is now shown that indole exists in the intestine of such rabbits; there is therefore no need to assume that the urinary indican arises elsewhere.

W. D. H.

Phenols, Free and United with Sulphur, in the Urine. L. MONFET (*Compt. rend.*, 1903, 137, 386—387).—In the intestine, indole and scatole originate from proteids, phenol and cresol from hydrocarbons (hydrocarbonés); these enter the body in part as ethereal sulphates. Indole and scatole potassium sulphates are easily decomposed by mineral acids and by oxalic acid, whilst phenol and cresol potassium sulphates, which are stated to be identical with those prepared synthetically, are not. On this is based a method of estimation in urine and faeces, and observations on more than two hundred pathological cases are promised. The faeces do not contain sulphur conjugated phenols; the urine contains only traces of free phenols which are retained by animal charcoal.

W. D. H.

Nuclein Metabolism in Lymphatic Leucæmia. YANDELL HENDERSON and GASTON H. EDWARDS (*Amer. J. Physiol.*, 1903, 9, 417—424).—In a case of lymphatic leucæmia of the chronic type, observations on the excreta show that during two periods in which observations were made the course of metabolism was somewhat different. In spite of the increase of leucocytes, the excretion of uric acid and phosphates was at no time excessive; the increase appears therefore to be due to the failure of the normal destructive processes. The diet was practically the same throughout and was almost nuclein-free. During one period, the specific gravity corresponded with the total nitrogen of the urine; during the second period, in which nitrogenous metabolism was greatly reduced, this was not so. During both periods, the total acidity varied directly as the nitrogen. The chlorides varied with the volume of water and showed more variation than any other substance estimated.

W. D. H.

Proteolytic Action of Kidney Enzyme. HENRY D. DAKIN (*J. Physiol.*, 1903, 30, 84—96).—The products obtained by the digestion in an acid medium of the finely divided kidney substance by the prolonged action of the enzyme that can be expressed from the kidney cells were examined. The fluid contained a small amount of coagulable proteid in solution, and a precipitate of paranuclein. Albumoses and peptone were practically absent. The tryptophan reaction with bromine water could not be obtained, after the first few days' digestion had occurred. The formation of ammonia extended over a period of two months; this is derived from substances of the nature of acid amides decomposable by hydrochloric acid, and not from the stable amino-acids. Other substances identified were alanine, α -aminoisovaleric acid, leucine, α -pyrrolidinecarboxylic acid, phenylalanine, tyrosine, lysine, histidine, cystin, hypoxanthine, and indole derivatives which, in some cases, gave the reactions of scatole-

aminoacetic acid. Possibly a small amount of glutamic acid was present, but arginine and aspartic acid were absent. W. D. H.

Urine of the Musk Rat. ROBERT BANKS GIBSON (*Amer. J. Physiol.*, 1903, 9, 391—395).—The nitrogenous metabolism of the musk rat (*Fiber zibethicus*) resembles quantitatively that of the guinea-pig, the average output per 100 grams of body weight being 0.1 gram of nitrogen. Most of this is in the form of urea (91—94 per cent.), uric acid accounts for 1.5 per cent., and this was raised by adding meat to the diet. The amount of ammonia is small as in other herbivora. The amount of phosphoric acid excreted is high; this is not the rule among herbivora. Allantoin did not appear after ingestion of nucleic acid, as is the case in the dog and cat. Kynurenic acid and creatinine were not found; proteids and sugar were also absent. Urobilin and at times bile pigment were present.

W. D. H.

Formation of Uric Acid in Birds. T. H. MILROY (*J. Physiol.*, 1903, 30, 47—60).—Hydrochloric acid given to birds in doses smaller than those which result in acid poisoning affects the uric acid synthesis, diminishing the transformation of ammonium salts into uric acid. The same occurs with lactic acid, but on neutralisation the effect is no longer produced. Galvanic stimulation of the liver aids the synthesis, and if acid is given also prevents the usual action of the acid. In the bird, the direct transformation of purine bases into uric acid is not an important mode of origin of that substance.

W. D. H.

Nuclein Bases of Fæces. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1903, 39, 199—202).—The question of the occurrence or not of important quantities of the purine bases in the fæces has been the subject of controversy. In the present research, it is shown that putrefaction is an important factor. As a result of auto-putrefaction in the fæces, all but a small residue of the bases disappears. It is believed that they are synthesised and built into the bodies of the bacteria.

W. D. H.

Urinary Indican. CH. PORCHER and CH. HERVIEUX (*Zeit. physiol. Chem.*, 1903, 39, 147—154).—Experiments are given on the urine of horse and dog which confirm Maillard's statement (*Abstr.*, this vol., ii, 563) that indigo-red is a derivative of indigo-blue. Rapid oxidation of indoxyl yields the blue, slow oxidation the red compound. These indoxyl derivatives were found to be constant constituents of the normal urine of horse, dog, rabbit, guinea-pig, and man.

W. D. H.

Excretion of Ammonium Urate and Sodium Indigotinsulphonate by the Serpent's Kidney. TRIBONDEAU (*Compt. rend. Soc. Biol.*, 1903, 55, 1130—1132).—The terminal portions of the uriniferous tubules in serpents' kidneys, in addition to forming the aqueous and mucous portion of the urine, are also concerned, as evidenced by histological examination, in the definite formation of ammonium urate, and in the excretion of sodium indigotinsulphonate if this substance is introduced into the blood stream.

W. D. H.

Indicanuria. HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1903, 39, 214).—Polemical against Scholz.
W. D. H.

The Reducing Substance in Cerebrospinal Fluid. OTTORINO ROSSI (*Zeit. physiol. Chem.*, 1903, 39, 183—189).—Several specimens of human cerebrospinal fluid obtained by lumbar puncture were examined. In all cases, the questionable reducing substance proved to be dextrose. In fluid removed some hours after death, this has disappeared owing, probably, to glycolysis.
W. D. H.

Extracts of Brain and Blood. SWALE VINCENT and WILHELM CRAMER (*Proc. physiol. Soc.*, 1903, x—xi; *J. Physiol.*, 30).—An aqueous extract of brain contains three depressor substances; one of these is insoluble in absolute alcohol, and its effect is not abolished by atropine; the other two are soluble in alcohol, and of these the effect of one is abolished by atropine, that of the other not. The alcoholic solution was evaporated to dryness and taken up again with alcohol, and the procedure repeated several times. This, however, does not entirely get rid of inorganic substances, and shows that the inorganic constituents are originally present in organic combination. By the addition of platinic chloride to the final alcoholic solution, crystals are obtained of a platinichloride of a choline derivative (dicholine anhydride?) and of ammonium platinichloride. The latter is apt to be mistaken for the choline salts as it crystallises in octahedra; similar extracts of normal blood yield the same kind of crystals, and also produce a fall of pressure when injected intravenously. The tests for choline in blood described by Mott and Halliburton are therefore regarded as fallacious.
W. D. H.

Pathology of Acute Rheumatism. E. W. AINLEY WALKER and J. HENRY RYFFEL (*Brit. Med. J.*, 1903, ii, 659—660).—The micrococcus associated with rheumatism is distinguished from similar forms by several reactions, among which is rapid production of acid. Its hæmolytic action is also considerable, and will account for the anemia of rheumatic fever. The albumose it produces in cultures causes pyrexia when injected into animals. The main point dealt with in the present paper, however, is the production of acid. The micro-organism produces in cultures large quantities of formic acid, and at least one other acid of the same group not yet identified, but probably acetic; the same acids also are obtainable from the urine of rheumatic patients. In normal urine, formic acid is absent or present only in traces. A litre of culture yielded 0.5 gram of formic acid; no other micrococcus so far investigated produces so much. The formic acid is believed to originate from the oxidation of *D*-lactic into formic and acetic acids within the bodies of the micro-organisms. The formic acid can be separated either as the sodium or iron salt.

In view of this discovery, it is interesting to note that in country folk-lore it is alleged that bee-keepers, who are frequently subjected to the action of formic acid, are peculiarly insusceptible to rheumatism. It is, moreover, anticipated that the beneficial action of salicylates in rheumatism may find a simple chemical explanation.

W. D. H.

Serum from Typhoid Convalescents. LAMING EVANS (*J. Pathol. Bacteriol.*, 1903, 9, 42—66).—From a study of the disease and its treatment in S. Africa, the conclusions are drawn that the serum of typhoid convalescents has no constant bactericidal value, and the age of the patient is not an important factor. The variations are extreme (from 2 to 300,000 units). The power of the serum to agglutinate has no relation to its bactericidal power, and persists longer during the convalescence of the inoculated than of the uninoculated. The shortest time taken to kill *Bacillus typhosus* is $2\frac{1}{2}$ hours. So-called bactericidal antityphoid serum exerts no bactericidal influence, on account of the absence of complement, and may even exert a fatal influence when injected during an attack of typhoid fever on account of the presence of immune bodies.

W. D. H.

Croton-immunity. MARTIN JACOBY (*Beitr. chem. Physiol. Path.*, 1903, 4, 212—223).—The subjects treated are (1) the physiological constitution of croton-hæmolyisin and its relationship to anti-hæmolyisin; (2) cellular immunity against croton, and the presence of a substance which acts inhibitingly on it in the gastric mucous membrane.

W. D. H.

Chemistry of Rigor Mortis. ANTON STEYRER (*Beitr. chem. Physiol. Path.*, 1903, 4, 234—246).—The experiments were made on rabbits, and von Fürth's nomenclature of the muscle proteids is employed. The normal relation of myosin to myogen is 19:79; von Fürth gives nearly the same number, 18:81. After prolonged tetanisation, the muscle plasma contains less myosin. The opposite is true in the degeneration that follows section of the nerves going to the muscles; the increase of myosin begins on the fourth day after the operation, and progresses as more marked degeneration sets in. The division of the tendon of a muscle does not markedly alter the relationships of the two proteids.

W. D. H.

Rigor Mortis. OTTO FOLIN (*Amer. J. Physiol.*, 9, 374—379).—*Rigor* may be produced in frogs' muscles by subjecting them to a temperature of -15° to -20° . The muscles, although stiff when thawed, were perfectly transparent, and there was no production of acid. They were irresponsive to stimuli. If the muscles are cooled to only -7° , they do not enter into *rigor*, and when carefully thawed are still irritable. From the stiffened muscles, muscle plasma can be prepared in the usual way, which clots like plasma prepared from fresh muscle. The *rigor* produced by cold is regarded as true *rigor mortis*, and the coagulation theory of this phenomenon is thereby considered to be disproved.

W. D. H.

Respiration in Phloridzin Diabetes. ARTHUR R. MENDEL and GRAHAM LUSK (*Amer. J. Physiol.*, 1903, 10, 47—56).—The calories lost in the urinary sugar are compensated for not by increased combustion of fat, but of proteid. After the injection of 5 grams of phloridzin subcutaneously, as much as 60 per cent. of its carbon may be eliminated in the urine. In the early stages of phloridzin diabetes,

the carbon in the urine derived from hydroxybutyric acid or other abnormal products other than sugar and phloridzin itself, is negligible.

W. D. H.

Action of Phloridzin. PERCY G. STILES and GRAHAM LUSK (*Amer. J. Physiol.*, 1903, 10, 67—79).—An experimental discussion of the nature of phloridzin diabetes. It is a total diabetes, that is, dextrose, within certain limits, cannot be burnt. Loewi's hypothesis of a blood-sugar combination is accepted with the addition that the sugar in such combination cannot be burnt. Phloridzin will decompose it and permit the elimination of sugar by the urine; any free dextrose unites with the combining radicle and is protected. If the quantity rises beyond this combining power, immunity from destruction is lost and the sugar burns. To produce phloridzin diabetes, animals with sound kidneys are essential; one experiment may damage the kidney, and in a second experiment the nitrogen dextrose ratio of 3·7 : 1 may be replaced by a ratio of 2·8 : 1. In this case, the kidney has lost the power of splitting a dextrose combination formed from a definite percentage of the proteid sugar, a compound which is always burnt in animals having the lower ratio.

W. D. H.

[**Acetone in Diabetes.**] J. LE GOFF (*Compt. rend.*, 1903, 137, 216—217).—The part played by acetone in diabetes is doubtful; it, however, occurs in the urine and expired air in grave cases only. In the case under observation, analyses by Lieben's method showed that in the expired air the amount excreted by the lungs in the 24 hours varied from 1·07 to 2·7 grams. The urine for the same time contained 1·2 grains. Mixed with acetone, there appear to be other organic substances which also give Lieben's reaction.

W. D. H.

Hæmochromatosis in Diabetes. JAMES M. BEATTIE (*J. Pathol. Bacteriol.*, 1903, 9, 117—129).—Attention is drawn to a widespread condition of pigmentation in various organs, associated with cirrhosis of the liver and diabetes mellitus. This is associated with degeneration changes in the cells of the pancreas (specially), liver, and other organs. The pigment appears, in the main, to be free from iron; it is considered to originate from hæmoglobin, and the whole condition is attributed to a toxic agent possibly derived from the intestine *via* the portal circulation.

W. D. H.

Production of Dextrose in Animal Tissues. CADÉAC and MAIGNON (*Compt. rend.*, 1903, 136, 1682—1684).—All the organs and tissues of the dog and horse can, in the normal state, enclose a small quantity of dextrose. This is formed in greater quantity during asphyxia, and that already formed disappears more slowly. This is a phenomenon of protoplasmic life, and is no longer seen in tissues killed by boiling water.

W. D. H.

Pigmented Atrophy of the Mucous Membrane of the Small Intestine of Malarial Origin. LEONARD ROGERS (*J. Pathol. Bacteriol.*, 1903, 9, 111—116).—In many cases of malaria in India, the

small intestine was markedly atrophied, and associated with this was a dark slaty pigmentation of its mucous membrane. The black pigment of malaria can be demonstrated in both the mucous and sub-mucous coats.

W. D. H.

Does Arsenic exist in the Organs of the Animal Economy? ARMAND GAUTIER (*Compt. rend.*, 1903, 137, 295—301. Compare Abstr., 1900, ii, 152, 226; 1902, ii, 517).—The author considers the amount of arsenic which could be introduced by means of reagents in the tests previously instituted by him in his search for arsenic in animal organisms. The question of the possible loss of arsenic in the examination is also considered. The fact that arsenic was found in certain organs but not in others shows that the method is not at fault and that arsenic does really occur constantly in certain parts of animals. The organs in which it has been found are the epidermis, brain, thyroid, and thymus, whilst it is absent in ordinary blood. It is notably present in fish, and this may be connected with the fact that sea-water is decidedly arsenical.

J. McC.

Enhydrina Poisoning. LEONARD ROGERS (*Proc. Physiol. Soc.*, 1903, iv—v; *J. Physiol.*, 30).—*Enhydrina Bengalensis* is the commonest of the poisonous sea-snakes. The minimal lethal dose is 0.05 milligram per kilo. for warm-blooded animals, that is, ten times as powerful as cobra venom. On intravenous injection of a small dose into a cat, the respiration slows and the blood-pressure falls; finally respiration ceases after respiratory convulsions, and the blood pressure, after a rise, continues to fall to zero. Paralysis is due to action on the respiratory centre and on the motor end plates, especially in the diaphragm. The blood is dark in colour and clots rapidly.

W. D. H.

Influence of Alkaloids on Oxidation. RAOUL DUPOUY (*Compt. rend. Soc. Biol.*, 1903, 55, 1000—1001).—The presence of quinine, morphine, atropine, and strychnine in the blood in amounts comparable to those which would occur there after the use of these alkaloids as medicaments does not interfere with the guaiacum test. The theories built on the supposition that in their presence the test gives negative results therefore fall to the ground. The error has arisen from the previous employment of acid solutions of the alkaloids; the disappearance of the reaction is due to the acid, not to the alkaloid.

W. D. H.

Chemical Constitution and Physiological Action of Morphine. ERNST VAHLEN (*Zeit. physiol. Chem.*, 1903, 39, 95—98. Compare Abstr., 1902, i, 727).—A reply to Bergell and Pschorr (this vol., ii, 503).

E. F. A.

Relative Toxicity of Distilled Water, Sugar Solutions, and Solutions of Single Constituents of Sea Water for Aquatic Animals. JACQUES LOEB (*Flüger's Archiv*, 1903, 97, 394—409).—Aquatic animals, in their behaviour with relation to dis-

tilled water, fall into three groups. The first, for example, *Fundulus*, contain those to which it is harmless. The eggs of this animal neither swell in distilled water, nor shrink when placed in salt solution. They are surrounded with an impermeable membrane. Osmotic conditions evidently are not the only ones which play a part in the life processes of such animals.

To the second group belong those animals or their tissues which are surrounded by a semipermeable membrane, which is easily permeable to water, and impermeable or only slightly permeable to many salts. The red corpuscles and sea-urchin eggs fall into this group. The effect of reagents is here purely mechanical, and are explained by diffusion of certain ions. The effect of various salts on contractile tissues comes mainly under this head.

Gammarus, a marine crustacean with which the majority of experiments recorded in this paper deals, is an instance of the third group. Distilled water is rapidly fatal, so also is a solution of sugar or common salt of osmotic pressure equal to that of the sea water it lives in. Isotonic solutions of other constituents of the sea water are even more toxic. No doubt in ordinary sea water the salts act antagonistically, and death is attributable to the discharge of ions from the living tissues.

W. D. H.

The Pigments of the Lepidoptera. I. M. (GRÄFIN) VON LINDEN (*Pflüger's Archiv*, 1903, 98, 1—89).—The present article relates to the pigments of *Vanessa io* and *V. urticae*. These are different to those previously described in other butterflies, for instance in the *Pieridae* by Hopkins. The pigments examined were those of the intestine, excrements, epithelial and other tissues, both in the pupa and the fully-formed animal. In spite of small differences, the pigment appears to be essentially the same throughout. Two chief modifications are present, the reduced form, which is carmine-red, and an oxidised form which is greenish-yellow. The chemical rays of the spectrum act as oxidising agents, and warmth causes the pigment to become reddish-brown. Its crystalline form and many of its reactions resemble those of bilirubin and hæmatoidin. Its absorption spectrum is like that of urobilin; the absorption bands in the ultra-violet were also mapped out. It gives the reactions of a proteid, and can be split into a colourless proteid and a coloured acid component which contains iron. The proteid has some of the characters of a proteose, some of those of a globulin, and some of those of a histone. The pigment also contains free sugar. It is believed not only to play the part of a respiratory pigment, but also to act as a reserve-material in metabolism. It appears to arise from the chlorophyll of the ingested food.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Formation of Proteids in Fungi. OSKAR LOEW (*Beitr. chem. Physiol. Path.*, 1903, 4, 247—250).—Mainly polemical. The chief point is that Czapek has stated that methylhydrazine can act as a source of nitrogen to *Aspergillus niger*. The author finds that this substance, like other hydrazines, is a protoplasmic poison. In Czapek's experiments, the culture medium contained sucrose also, and was heated from 5—7° to 28° to ensure sterility; by this means, the sucrose would be inverted and hydrazones formed which are less toxic to living cells than unchanged hydrazines.

W. D. H.

Formation of Proteids in Plants. EMIL GODLEWSKI (*Bull. Acad. Cracow*, 1903, 6, 313—380).—When kept in darkness, higher plants, as well as fungi, produce proteids from nitrates and from the decomposition products of proteids; but in the case of higher plants the assimilation is restricted in absence of light. The energy required for the assimilation of nitrogen and the production of proteids, in absence of light, is furnished by metabolism and respiration. The relatively greater metabolism in fungi, as compared with higher plants, enables nitrogen assimilation to take place quite independently of light.

The most prominent non-proteids in seedlings of wheat and barley, three weeks old, were amino-acid amides (chiefly asparagine) and amino-acids; nitrogen compounds, precipitated by phosphotungstic acid, were present in smaller and generally varying quantities.

Root production, in the case of wheat and barley, was increased in relation to the upper parts of the plants when the amount of nitrogen was deficient.

N. H. J. M.

Action of Emulsin on Salicin and Amygdalin. VICTOR HENRI and S. LALOU (*Compt. rend.*, 1903, 136, 1693—1694).—From a study of experiments on the action of emulsin on the two glucosides mentioned, the theory is deduced that the ferment forms an intermediate additive compound with the glucoside, which then undergoes decomposition, liberating the ferment once more. A similar view is held regarding the *modus operandi* of trypsin.

W. D. H.

A Soluble Ferment in Vegetables which reduces Nitrates. J. E. ABELOUS and JULES ALOY (*Compt. rend. Soc. Biol.*, 1903, 55, 1080—1082).—Abelous and Gérard showed that a soluble ferment exists in the animal organism which is able to transform nitrates into nitrites and nitrobenzene into aniline. The present preliminary note states that the same is true for vegetable structures, the potato being the plant used.

W. D. H.

Fermentative Decomposition of Thymo-nucleic Acid by Fungi. LEONID IWANOFF (*Zeit. physiol. Chem.*, 1903, 39, 31—43).—Various fungi (*Aspergillus*, &c.) decompose nucleic acid with the

liberation of phosphoric acid and purine bases; this appears to be a ferment action; it is doubtful whether it is produced by the ordinary proteolytic ferments present, and the name *nuclease* is suggested for the enzyme responsible for the action.

W. D. H.

The Solution by Micro-organisms of Sodium α -Nucleate. H. PLENGE (*Zeit. physiol. Chem.*, 1903, 39, 190—198).—A large number of micro-organisms were examined, and the details concerning each are given in tabular form. Some render sodium α -nucleate and gelatin fluid; some liquefy one substance and not the other. The effect on nucleic acid appears to be due to a special enzyme. A specially valuable result is a new method of diagnosis between the colon bacillus and that of typhoid fever. Neither of them liquefy gelatin, but the liquefying effect on the nucleate is much more rapid in the case of the *Bacillus coli*.

W. D. H.

Decomposition of Yeast Nucleic Acid by Bacteria. I. ALFRED SCHITTENHELM and F. SCHRÖTER (*Zeit. physiol. Chem.*, 1903, 39, 203—207).—The action of micro-organisms (a pure culture of *Bacillus coli* from fæces was used) on yeast nucleic acid is to split off purine bases from it. Whether a special enzyme is responsible for this is left uncertain.

W. D. H.

Nitrifying Organisms. E. BOULLANGER and L. MASSOL (*Ann. Inst. Pasteur*, 1903, 17, 492—515).—The best temperature for cultivating nitrous and nitric organisms is 37°. The former are killed by heating at 45° for five minutes, the latter at 55°. The activity of the nitrous organism is increased by the presence of porous porcelain and especially by slag. The effect is less marked in the case of the nitric organisms and was only observed when slag was present. Rotation in a drum is also favourable.

The nitrous organism becomes less active when it has produced 8—10 grams of magnesium nitrite per litre, and its action ceases after the production of 13—15 grams. Potassium and sodium, and, in a less degree, calcium and magnesium nitrites, hinder the multiplication of the nitrous organism. Small amounts (0.1 to 0.5 per cent.) of sodium and potassium nitrates hinder the development of nitrous organisms, whilst the same result is only produced by at least 1 per cent. of calcium and magnesium nitrates.

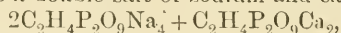
The conversion of nitrites into nitrates becomes more difficult as the amount of nitrite increases and stops altogether when the solution contains 2 per cent. of nitrite. The same effect is produced by 2.5 per cent. of sodium nitrate. Calcium nitrate retards nitrification when the solution contains 12 grams per litre.

N. H. J. M.

Properties and Composition of the Reserve Phospho-organic Substance of Chlorophyllous Plants. SWIGEL POSTERNAK (*Compt. rend.*, 1903, 37, 337—339. Compare this vol., ii, 607).—The phospho-organic substance obtained from tubers, &c., as a mixture of acid salts of magnesium, calcium, iron, and manganese yielded an acid having the composition indicated by the formula

$C_2H_8O_9P_2$, which differs from the one previously given by half a mol. of water. The acid dissolves in water in all proportions, is soluble in alcohol, insoluble in ether, benzene, chloroform, and glacial acetic acid. It does not crystallise, but thickens when cooled to -23° ; when heated at 100° , it becomes brown.

The acid is at least tetrabasic, but the only crystalline salt which could be obtained is a double salt of sodium and calcium,



with $8H_2O$.

The acid completely precipitates animal and vegetable proteids in neutral or acid solutions.

N. H. J. M.

Constitution of the Phospho-organic Acid of the Reserve Substance of Green Plants. First Product of the Reduction of Carbon Dioxide in Chlorophyllous Assimilation. SWIGEL POSTERNAK (*Compt. rend.*, 1903, 137, 439—441. Compare preceding abstract).—When heated with dilute mineral acids, the acid $C_2H_8O_9P_2$ is converted quantitatively into inositol and phosphoric acid. Treatment with benzoyl chloride failed to indicate the presence of alcoholic hydroxyl, and the acid has probably the constitution represented by the formula $O[CH_2 \cdot O \cdot PO(OH)_2]_2$, and may be termed *anhydro-oxymethylenediphosphoric acid*.

The conclusion is drawn that the organic group associated with phosphoric acid is produced in the reduction of carbon dioxide, and that it is not capable of existing in the free state. Under normal conditions, it is utilised in the production of carbohydrates, proteids, and the foregoing phospho-organic acid, &c. If not utilised in this manner, it is converted into inositol, which is found almost exclusively in the green portions of plants.

N. H. J. M.

Proteolytic Ferment of Malt. PHILIP SCHIDROWITZ (*J. Fed. Inst. Brewing*, 1903, 9, 361—382).—Readily assimilable nitrogen retards, and sometimes entirely inhibits, the formation of the gelatin-liquefying proteolytic enzyme, and it is probable that the secretion of the enzyme is, like that of diastase, a starvation phenomenon (Brown and Morris, *Trans.*, 1890, 57, 497). Sucrose also has an inhibitive action. There is evidence that the specific action of asparagine and ammonium nitrate is very slight, the retardation produced being due to the non-formation of the enzyme.

As regards the influence of the composition of the steeping liquor on the quality of malt, it was found that gypsum has a tendency to restrict slightly the development of the enzyme.

No clearly defined connection seems to exist between proteolytic power and the constituents of malts usually determined. Higher-dried malts have a lower proteolytic power, and a low proteolytic power observed in one of the samples examined may be connected with the relatively low percentage of non-coagulable proteids.

N. H. J. M.

Effect of Heating on the Solubility of Nitrogenous Food Constituents in Pepsin-hydrochloric Acid. JAKOB VOLHARD (*Landw. Versuchs-Stat.*, 1903, 58, 433—437).—The digestibility-coefficient

of proteids decreases as the temperature at which the substance has been dried rises, but the decrease is immaterial when the temperature does not exceed 60°. Digestibility is also diminished when foods which have been produced at high temperatures, such as brewers' grains, are dried.
N. H. J. M.

Feeding Experiments on the Utilisation of Rye and Wheat Brans of Different Degrees. ALBIN KÖHLER, F. HONCAMP, M. JUST, JAKOB VOLLIARD, and G. WICKE (*Landw. Versuchs-Stat.*, 1903, 58, 415—432).—The results of feeding experiments with sheep showed that bran which contains distinct amounts of meal has a greater value than when free from meal. In the case of rye, the nitrogenous constituents of the bran containing meal are somewhat less than in bran free from meal, but this is more than counterbalanced by the greater amount of readily digestible carbohydrates present in the meal.
N. H. J. M.

Mechanical Analysis of Soils. THÉOPHILE SCHLOESING, sen. (*Compt. rend.*, 1903, 137, 369—374).—The soil (10—12 grams) is treated successively with dilute nitric acid and distilled water rendered slightly ammoniacal, and the coarser sand is removed by washing and decantation; the decanted liquid is then poured into an apparatus (figured in the original) by means of which the successive sediments can be separated and afterwards weighed. The process requires some attention at first to avoid stoppage of the apparatus by the coarser particles, but after a time it can be left, the deposits being received in a series of capsules drawn into position by clockwork.

Nine deposits were obtained, the time between each increasing from 5 minutes to 10 hours 40 minutes. Results obtained with a number of soils showed that the limits of size in the different deposits were as follows: (1) 90—70; (2) 80—65; (3) 70—50; (4) 50—30; (5) 35—20; (6) 20—15; and (7 to 9) 15—5 thousandths of a mm. The substance remaining in suspension after 21 hours and 20 minutes is considered to be clay.
N. H. J. M.

Mechanical Analyses of Soils. THÉOPHILE SCHLOESING, sen. (*Compt. rend.*, 1903, 137, 398—402).—Results of mechanical analyses of three soils by the method previously described (compare preceding abstract).
N. H. J. M.

Manurial Experiments with Tobacco. MAX LEHMANN (*Landw. Versuchs-Stat.*, 1903, 58, 439—470).—Whilst nitrogen seems to be equally required by all parts of the tobacco plant, potassium seems to be of use chiefly to the leaves and roots, and phosphoric acid to the stems.

Excessive manuring is to be avoided, as it increases the amount of water in the leaves and promotes a relatively greater development of stems and roots. Chlorides and sulphates are unsuitable, as they decrease the burning properties of tobacco. Potassium carbonate and "martellin" act favourably in this respect.

Perchlorate does not act poisonously on tobacco, when present in

moderate quantity, but favours the development of the leaves and especially the roots.

N. H. J. M.

Estimation of Free Phosphoric Acid. Amount present in Superphosphates. ARMAND-DEZSÖ HERZFELDER (*Landw. Versuchs-Stat.*, 1903, 53, 471—479).—The substance (1 gram) is extracted with dry ether for 10 hours in a Soxhlet apparatus. After distilling off the ether, the residue is treated three times with 20 c.c. of water. The filter is washed out with water containing a little methyl-orange as long as a red coloration is produced.

When superphosphates contain less than 3.55 per cent. of free acid, corresponding with 0.5 c.c. of normal alkali, a larger quantity should be employed. The titration may be repeated, using phenolphthalein. In absence of any combined acid, the two titrations do not differ by more than 0.05 c.c.

Results of analyses made with 53 superphosphates showed that the amounts of free acid varied from 0.53 to 10.65 per cent., and that the English and French superphosphates contained much less free acid than those prepared in Hungary and Germany.

N. H. J. M.

Analytical Chemistry.

New Volumetric Method of General Applicability. LAUNCELOT W. ANDREWS (*Zeit. anorg. Chem.*, 1903, 36, 76—83).—When chlorine water is added to a neutral solution of potassium iodide until the chloroform used as indicator is decolorised, reaction takes place according to the equation: $KI + 3Cl_2 + 3H_2O = KCl + HIO_3 + 5HCl$, but if a large excess of hydrochloric acid is present, the reaction takes place according to the equation: $KI + Cl_2 = KCl + ICl$. In both cases, the end point of the reaction is sharp. The reaction of potassium iodate on potassium iodide is similarly dependent on the amount of acid present; if there is a large excess of acid, the reaction takes place according to the equation: $2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O$, and this reaction is used in the estimation of iodides, free iodine, chromates, chlorates, antimony, arsenic, and iron. In the estimation of an iodide, so much concentrated hydrochloric acid is added that after titration there will be not less than 15 per cent. present; about 5 c.c. of chloroform are added, and the solution is titrated in a stoppered bottle with 1/10 or 1/5*N* potassium iodate solution until the chloroform is decolorised and the aqueous solution is yellow, on account of the presence of dissolved iodine chloride. In the estimation of oxidising compounds, a known excess of potassium iodide is first added, and the same method employed in order to determine the excess which has been taken. For the estimation of the antimony and arsenic, no

potassium iodide need be added, because the reaction takes place according to the equation: $2\text{ACl}_3 + \text{KIO}_3 + 5\text{H}_2\text{O} = 2\text{H}_3\text{AO}_4 + \text{KCl} + \text{ICl} + 4\text{HCl}$, where $\text{A} = \text{Sb}$ or As . J. McC.

Electrochemical Analysis and the Voltaic Series. J. E. Root (*J. Physical Chem.*, 1903, 7, 428—465).—The author has determined the decomposition voltage of salts of silver, mercury, copper, antimony, bismuth, hydrogen, lead, zinc, cobalt, and nickel in solutions of oxalates, phosphates, ammoniacal tartrates, and cyanides. Tables of the results are given, and afford data necessary for determining the conditions of separation of the various metals, and the bearing of the results on methods of electrochemical analysis is briefly discussed. The decomposition voltage of silver is nearly a volt higher than that of mercury in double cyanide solutions; the metals cannot, however, be separated, as silver is precipitated with the mercury. It was indicated that nickel could be readily separated from cobalt in alkaline tartrate solution, and experiments proved that the separation is very satisfactory. L. M. J.

Bomb-calorimeter and Method of its Use. WILBUR O. ATWATER and J. F. SNELL (*J. Amer. Chem. Soc.*, 1903, 25, 659—699).—This description of a modification of Berthelot's process is unsuitable for abstraction. The chief point of difference between this calorimeter and Berthelot's apparatus is that whereas the cover of the Berthelot fits into the cylindrical cup like a very wide stopper, the cover of the improved apparatus rests directly on the rim of the cup. For reasons of economy, the platinum lining is replaced by one of copper heavily electroplated with gold. L. DE K.

A Method for Calibrating Burettes. DAVID W. HORN and ELIZABETH M. VAN WAGENER (*Amer. Chem. J.*, 1903, 30, 96—105).—Two burettes, one of which has been calibrated by the usual method, are supported vertically, and connected below by indiarubber tubing. One is kept stationary, and water caused to flow into it by raising the other. A duplicate calibration is obtained by reversing the process. C. H. D.

Cyanogen Iodide as an Indicator for Acids. JOSEPH H. KASTLE and MARY E. CLARK (*Amer. Chem. J.*, 1903, 30, 87—96).—Cyanogen iodide reacts with potassium iodide in moderately concentrated solutions, setting free iodine. At dilutions of $N/100$ and upwards, however, no reaction occurs in neutral solution, but iodine is at once set free on the addition of an acid, and a solution of cyanogen iodide, potassium iodide, and starch may therefore be used as an indicator for dilute acids. The sensitiveness is equal to, or slightly greater than, that of litmus or phenolphthalein, and is as great for the weaker organic acids as for strong acids. A solution containing 77 parts of CO_2 per million gives a distinct reaction. The indicator may also be employed to determine the degree of hydrolysis of salts such as alum at high dilutions, the blue tint produced being compared with that given by a sulphuric acid solution of known concentration. C. H. D.

***p*-Nitrophenol as Indicator.** ALWIN GOLDBERG and K. NAUMANN (*Zeit. angew. Chem.*, 1903, 16, 644—647).—An alcoholic solution of *p*-nitrophenol, or an aqueous solution of its sodium derivative, may be substituted for methyl-orange in volumetric work. The yellow colour of the dissolved sodium derivative is discharged by acids and restored by alkalis. A comparatively large quantity of the nitro-compound is required in order to obtain a definite end reaction with the strong acids. This indicator is not very serviceable in the case of the weaker acids and sulphurous acid, and for carbonates it is, perhaps, less delicate than methyl-orange. The results of similar experiments made with 5-nitrosalicylic acid (*p*-nitrophenol-*o*-carboxylic acid) were even less satisfactory.

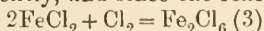
L. DE K.

Use of Normal Sodium Oxalate in Volumetric Analyses. S. P. L. SÖRENSEN (*Zeit. anal. Chem.*, 1903, 42, 333—359).—The author's earlier experiments (*Abstr.*, 1898, ii, 185) were made by the ordinary methods of volumetric analysis, which were not sufficiently delicate to indicate whether sodium oxalate could be employed in standardising acids in cases where the highest attainable accuracy was required. In the present series, methods were adopted which reduced the errors of experiment to much narrower limits. The oxalate (8—12 grams) was weighed with a maximum error of 1/80000, the acid to within 1/20000; all weighings were by Gauss's double method, and were reduced to vacuum. Under these conditions, the mean error of an estimation was only 1/24400 of the total quantity, and the greatest deviation from the mean was 1/13200. The method of igniting the oxalate influences the results slightly. Rapid ignition with limited access of air always gives a residue containing carbon, which obstinately retains some alkali. By igniting at a lower temperature, and with freer access of air, the separation of carbon can be almost entirely prevented. The best method of preparing the oxalate is to add a small excess of sodium carbonate to a solution of oxalic acid, concentrate, and cool. The crystallised salt is dried at 100° to decompose sodium hydrogen carbonate, and again crystallised. It is then dissolved in hot water and precipitated by alcohol. This salt retains a small quantity of water, which is not expelled at 150°. By drying at 240—250°, the water is removed completely, and the dry salt is not hygroscopic. Attempts to prepare a salt containing water of crystallisation failed altogether. Pure sodium oxalate gives no colour to concentrated sulphuric acid, whereas the organic impurities most likely to be present would give a brown coloration. The purest sodium oxalate obtainable is feebly alkaline to phenolphthalein; the alkalinity of its aqueous solution increases on boiling, or even on warming, the solution. These results show that when care is taken to use a pure and dry salt, and to ignite slowly, results can be obtained of sufficient accuracy for the most refined purposes.

M. J. S.

Critical Studies on the Volumetric Estimation of Iron by Permanganate. A. SKRAJAL (*Zeit. anal. Chem.*, 1903, 42, 359—405).—The first part of this paper is devoted to a theoretical and experimental study of the titration of ferrous salts in presence of hydrochloric acid

and chlorides. Adopting Manchot's theory of the formation of a "primary oxide," Fe_2O_5 , as the first effect of the action of permanganate on a ferrous salt (Abstr., 1903, ii, 151, 152), it is evident that when the "acceptor" hydrogen chloride is present, the two reactions, $\text{Fe}_2\text{O}_5 + 4\text{FeO} = 3\text{Fe}_2\text{O}_3$ (1), and $\text{Fe}_2\text{O}_5 + 4\text{HCl} = \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{Cl}_2$ (2), will take place concurrently, and since the reaction



proceeds more slowly, chlorine will be evolved, and more permanganate will be reduced than corresponds with the ferrous iron present.

The larger the amount of hydrochloric acid in proportion to the iron, the more favourable is the condition for the occurrence of the second reaction. The addition of metallic chlorides to a ferrous solution acidified with sulphuric acid has a similar effect in increasing the consumption of permanganate, although it is noteworthy that the increase is smallest in the case of mercuric chloride, which is electrolytically dissociated to a less extent than the chlorides of the alkali metals. The addition of sulphates (with the exception of ammonium sulphate) to a solution acidified with hydrochloric acid decreases the excess of permanganate consumed; manganous sulphate, in sufficient quantity, practically counteracts the effect of a moderate amount of hydrochloric acid, especially if phosphoric acid is also present, since manganic phosphate appears to be incapable of oxidising hydrochloric acid, although it oxidises ferrous salts.

The second part of the paper deals with the methods of reducing ferric solutions. It is shown that the reduction of ferric salts by stannous chloride, with the removal of the excess of stannous chloride by mercuric chloride, is by no means so accurate as hitherto supposed, since the suspended mercurous chloride acts as an acceptor and consumes an appreciable amount of permanganate.

On these grounds, the excess of stannous chloride should be kept as small as possible. If zinc is used for the reduction, it is necessary not only to filter the reduced solution, but also to prove that the solution of the zinc in sulphuric acid is free from substances capable of acting as acceptors. Sulphurous acid and hydrogen sulphide are less satisfactory.

For standardising a permanganate solution, the best substance is pure metallic iron. The iron obtained by electrolysis of ferrous ammonium oxalate (Treadwell and Classen) is not free from carbon, even when a current of less than 4 volts is employed, and the results obtained with it show considerable discordances. A much purer iron is obtained by the electrolysis of a neutral solution of pure ferrous ammonium sulphate with an anode of platinum foil on which iron has previously been deposited from Classen's oxalate solution. A current of only a few hundredths of an ampere, and 0.3—0.4 volt is used. With such iron, the results are very concordant. Taking them as a standard and calculating from them the results of the titration of Classen's iron, it appears that the latter may contain impurities amounting to 1.5 per cent. Iron wire of known composition may also be used, but as the solution of such iron contains other oxidisable substances, and the undissolved iron carbide also reduces permanganate, it is necessary to work in the following manner. The solution of the iron in sulphuric

acid is treated with a quantity of permanganate insufficient for complete oxidation; it is then exposed to air until the carbide has completely disappeared, and is finally reduced either with zinc, or with hydrochloric acid and stannous chloride. In the latter case, a correction for the permanganate consumed by mercurous chloride under the same conditions must be made. The iron wire may also be dissolved in hydrochloric acid and oxidised with chlorate, then reduced with stannous chloride as before. In this case, no correction for calomel seems required, the cause being apparently that the last traces of chlorine are not removed either by boiling or by the action of the stannous chloride. If the iron wire contains copper, this must be calculated as iron, since cupric salts are reduced by stannous chloride. M. J. S.

Titration with Potassium Iodate. LAUNCELOT W. ANDREWS *J. Amer. Chem. Soc.*, 1903, 25, 756—761).—The process is based on the fact that if potassium iodate is added to a solution of iodine in a liquid containing a considerable excess of hydrochloric acid, the iodine will be gradually converted into iodine monochloride. The end of the reaction may be ascertained by using chloroform as the indicator.

On adding a solution of potassium iodate to reducing agents dissolved in dilute hydrochloric acid, free iodine is liberated, which, however, on treatment with more of the reagent will again disappear. In this manner, accurate titrations may be made of iodides, arsenious acid, antimonious compounds, and even ferrous sulphate. With the iodides, the reaction is represented by the equation: $2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O$, whilst in the case of the arsenious solution, the following change occurs: $2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + KCl + ICl + 4HCl$. Since the reaction is not interfered with by the presence of copper, the process may be employed in the analysis of Paris green.

The process may be also used for the indirect titration of chromates and chlorates by decomposing these compounds with potassium iodide in the presence of sufficient hydrochloric acid and titrating the liberated iodine. L. DE K.

Lead Dioxide as Absorbent in Ultimate Analysis. MAXIMILIANO DENNSTEDT and F. HASSLER (*Zeit. anal. Chem.*, 1903, 42, 417—427).—Dennstedt formerly stated that lead dioxide only absorbed the oxides of nitrogen completely in the presence of moisture, and recommended that the portion of the combustion tube containing the dioxide should be kept cool during the combustion. This is now found not to be correct.

Incomplete absorption is due to a temporary absence of an excess of oxygen, nitric oxide then passes over the lead dioxide and is subsequently oxidised to nitric acid in the calcium chloride tube. If, however, care is taken that an excess of oxygen is always present, the absorption of the resulting nitrogen tetroxide is absolutely complete, both at low and high temperatures, and in the absence or presence of moisture.

Sulphur dioxide is absorbed with equal completeness, but when sulphur trioxide is present it is necessary to keep the lead dioxide at 200—300°. A temperature of 260—280° is also necessary for the absorption of chlorine, bromine, and their hydrogen acids, but above

450° the resulting lead oxychloride and oxybromide sinter and cannot readily be decomposed by treatment with an alkali carbonate. By keeping the temperature at about 350° and then warming the contents of the boats with a 20 per cent. solution of potassium hydroxide, the chlorine, bromine, and sulphuric acid are easily and completely extracted as potassium salts. At this temperature, also, there is no danger of the reduction of the lead dioxide to monoxide, or of the retention of carbon dioxide.

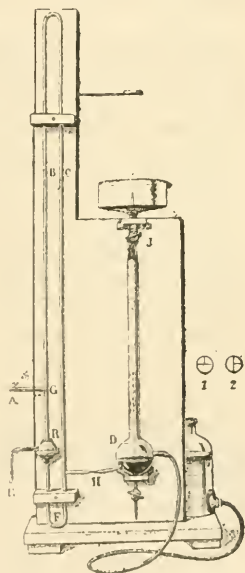
M. J. S.

Apparatus for the Estimation of Nitrogen. R. MARQUIS (*Bull. Soc. chim.*, 1903, [iii], 29, 780—781).—The two upright tubes are connected together at both ends, and one of the vertical branches has two side-tubes, the upper one leading to the combustion tube whilst the lower, which is connected with the pump, is opened or closed by means of the three-way tap *R*. The other upright tube is connected with a collecting tube, the latter having a bulb at its lower extremity partly filled with mercury. The tap being in position 1, the apparatus is exhausted, and after closing the tap the carbon dioxide is set free in the ordinary way until the air is displaced; this operation is repeated and finally mercury is drawn up the vertical tube to the level of *G*, and the tap *R*, which is now below the mercury, is closed so that any leakage at this point is prevented, and the analysis is then conducted in the ordinary way, the nitrogen passing out in the direction *A*, *G*, *B*, *C*, *H*.

L. DE K.

Estimation of Nitrogen by Kjeldahl's Method. FRIEDRICH KUTSCHER and H. STEUDEL (*Zeit. physiol. Chem.*, 1903, 39, 12—21).—In using this method for estimating the nitrogen in creatine, creatinine, lysine, and histidine, low results were obtained, especially when potassium permanganate was employed to aid the oxidation of the substance with sulphuric acid, thus confirming the well-known fact that the addition of permanganate causes a loss of nitrogen (compare *Trans.*, 1895, 67, 811). In some cases, also, the addition of an excess of copper sulphate gave rise to low results.

W. P. S.



Kjeldahl's Method. BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1903, 98, 130—134).—The statement of Kutscher and Steudel (compare preceding abstract) that Kjeldahl's method for the estimation of nitrogen is not trustworthy for creatine and other substances of physiological importance is combated. A large number of analyses from the author's own work and that of Argutinsky are given, which show that the method is a most exact one except for those nitro- and cyanogen compounds which have long been known not to yield all their nitrogen as ammonia in the process.

Some suggestions are made why Kutscher and Steudel obtained their faulty results.
W. D. H.

Estimation of Ammonia. ALEXANDER BAYER (*Chem. Zeit.*, 1903, 27, 809—810).—The process, which is intended for liquids containing besides ammonium salts also nitrogenous compounds likely to yield ammonia on distillation, is as follows: 200 c.c. of the liquid are mixed with a little fuming hydrochloric acid, 2 drops of phenolphthalein are added, and then an excess of magnesium chloride. After adding 12 grams of disodium phosphate, the liquid is mechanically stirred while aqueous sodium hydroxide is slowly added until a permanent rose colour is produced. After 15 minutes, the precipitate, which contains the magnesium ammonium phosphate, is collected at the pump and the well-drained mass is then distilled with water and some magnesia in order to set free the ammonia.
L. DE K.

Estimation of Ammonia in Urine. MARTIN KRÜGER and O. REICH (*Zeit. physiol. Chem.*, 1903, 39, 165—182).—Würster's method of removing the ammonia by distillation under reduced pressure is recommended; the frothing, which usually occurs, may be avoided by the addition of a small amount of alcohol. Magnesia usta should not be used, as it slowly decomposes certain complex nitrogenous substances present, yielding small amounts of ammonia. Milk of lime and baryta do not possess this disadvantage.

Urines containing proteids are best treated with Esbach's reagents in the finely-divided solid state (1 gram of citric and 0.5 gram of picric acid for 100 c.c. of urine) before the ammonia is estimated.

The results obtained appear to indicate that the total nitrogen in urine usually bears a constant relationship to the ammoniacal nitrogen.

J. J. S.

Estimation of Ammonia in Urine, Fæces, Blood, &c. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1903, 39, 73—80).—The following method is proposed. From 25 to 50 c.c. of the liquid are placed in a distillation flask, to which are then added about 10 grams of sodium chloride and sufficient sodium carbonate to render the solution distinctly alkaline. Solid substances may be rubbed down in a mortar with a little dilute hydrochloric acid, and then made up to bulk. The flask is placed in a water-bath and connected with an absorption tube containing 10 to 30 c.c. of $N/10$ acid and surrounded by ice. The absorption tube in its turn is connected with a water-pump. After removing the air from the flask and absorption tube as far as possible, about 20 c.c. of alcohol are run into the flask, and, when this has been evaporated under reduced pressure, further small quantities of alcohol are added and evaporated. The temperature of the water-bath holding the flask should be about 43° . The titration of the acid in the absorption tube is then carried out as usual. Results are given to show that the method is trustworthy (compare Abstr., 1903, ii, 239).

W. P. S.

Analysis of Human Urine. WILLIAM CAMERER, MEINHARD PFAUNDLER, and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1903, 45, 1—22).—In pure

solutions of urea, practically identical results were obtained by analyses carried out by Hufner's and Kjeldahl's methods. The addition of a mixture of phosphotungstic and hydrochloric acids makes no difference to the results. A number of analyses of normal human urine on different diets, and of others from pathological cases, follow. The different forms in which the nitrogen appears (urea, ammonia, purine compounds, &c.) are given, but the results present little of general interest.

W. D. H.

Estimation of Ammonia in Wine, and its Rôle in the Differentiation of "Mistelles" from Sweet Wines. J. B. VINCENT LABORDE (*Compt. rend.*, 1903, 137, 334—336).—The author has compared the method recently suggested by Gautier and Halphen (this vol., ii, 564) for the estimation of ammonia in alcoholic liquors with the Müntz method adopted in 1898 (*Ann. Inst. Pasteur*, 1898, 517), and finds that by the two methods the same amount of ammonia is obtained, and thus his former results are confirmed. The increase of volatile cyclic bases as fermentation proceeds, as found by Gautier and Halphen for wines from the South of France, does not take place with Bordelais wines. Duclaux's opinion that the ammonia naturally occurring in the must is utilised by the ferment has been confirmed, but, depending on various conditions, some ammonia may remain after the fermentation is complete.

The author does not agree with Gautier and Halphen that the maximum amount of ammoniacal nitrogen in sweet wines is 10 milligrams per litre; he has found as much as 16 to 25 milligrams per litre of ammoniacal nitrogen in Sauterne wines. J. McC.

Estimation of Ammoniacal Nitrogen in "Mistelles" and Wines. ALBERT DESMOULIÈRE (*J. Pharm. Chim.*, 1903, 18, 203—206).—Three to five hundred c.c. of the sample of the wine or "mistelle" (grape juice mixed with alcohol) are mixed with excess of magnesium oxide, a few drops of oil are added to prevent frothing, and the liquid is distilled at 35° under diminished pressure. The vapours are condensed in a receptacle containing about 50 c.c. of *N*/10 sulphuric acid and placed in cold water. The distillation is continued until the distillate is equal in bulk to half the volume of the sample originally taken.

The distillate is then redistilled with the addition of an excess of sodium hydroxide, and the vapours are condensed in a measured volume of *N*/50 sulphuric acid. After boiling to expel traces of carbon dioxide, the excess of acid is titrated with *N*/50 alkali, using litmus as indicator. L. DE K.

Differentiation between "Mistelles" and Liqueur Wines. GEORGES HALPHEN (*Ann. Chim. anal.*, 1903, 8, 246—252, 291—295).—A process for differentiating between non-fermented grape juice preserved with alcohol, or so called "mistelles," and duly fermented liqueur wines. Advantage is taken of the fact that the fermentation process affects the proportion between dextrose and levulose, gives rise to the formation of glycerol, increases the volatile acidity, and causes a

large diminution in the ammoniacal nitrogen. Tables are given illustrating the difference. The amount of volatile acid, glycerol, and sugars present is ascertained by the usual processes. The estimation of the ammoniacal nitrogen is carried out as follows:

Three hundred c.c. of the sample are mixed with dilute sulphuric acid until a green coloration is obtained with methyl-violet, the liquid is then evaporated to expel the alcohol, and when cold diluted to the original volume. A known sufficient volume of a 10 per cent. solution of lead acetate is added, and as much as possible of the filtrate is collected in a graduated measure. The liquid is transferred to a distilling flask, the lead is precipitated with solution of sodium sulphate, 10 grams of magnesium oxide are added, and the distillate is condensed in a receptacle containing 5 c.c. of hydrochloric acid. When the distillate is no longer alkaline, the acid is evaporated just to dryness and the residue is treated with excess of platinic chloride. The whole is again evaporated to dryness and the excess of platinic chloride removed by alcohol of 80 degrees (French). The ammonium platinichloride is finally ignited with the usual precautions and weighed as metallic platinum, from which the nitrogen is then calculated. The solubility of ammonium platinichloride in alcohol of 80° is about 1 in 15,000.

L. DE K.

Estimation of Nitric Acid in Water. ARTHUR MILLER (*Zeit. angew. Chem.*, 1903, 16, 746—747).—The process is based on the fact that nitrates are completely converted into chlorides by evaporation with a large excess of hydrochloric acid. The chloride may then be titrated with standard silver nitrate, allowance being made for chlorides already present in the liquid. The results are satisfactory when the amount of nitrate exceeds that of the chlorides.

In applying the process to water analyses, it would be necessary first of all to evaporate to dryness in the presence of an appropriate amount of barium chloride in order to eliminate earthy and alkali carbonates. The greater portion of any large excess of chloride might be removed with silver sulphate.

L. DE K.

Estimation of Sulphur by Hydrogen Peroxide. JULIUS PETERSEN (*Zeit. anal. Chem.*, 1903, 42, 406—417).—The sulphur in certain organic compounds can be quantitatively oxidised to sulphuric acid by hydrogen peroxide in alkaline solution. As the reaction takes place equally well in alcoholic (alkaline) solution, substances insoluble in water can be treated by this method. The method is very serviceable for the estimation of sulphur in gunpowder, the powder being boiled with sodium hydroxide and the solution treated while warm with hydrogen peroxide, then boiled, acidified, filtered, evaporated to expel nitric acid, and precipitated with barium chloride.

Another method is based on the solubility of sulphur in sodium sulphite and the separation of the resulting thiosulphate from the excess of sulphite by strontium nitrate, as suggested by Autenrieth and Windaus (*Abstr.*, 1898, ii, 452). The two methods give identical results. Many organic substances, however, such as thiophen, ethyl

sulphide, phenyl mercaptan, and ethyl thiocyanate yield no sulphuric acid when treated with alkaline hydrogen peroxide. M. J. S.

Estimation of Sulphuric Acid in Presence of Zinc. ALFRED THIEL (*Zeit. anorg. Chem.*, 1903, 36, 84—87).—In presence of zinc ions, sulphuric acid is not completely precipitated as barium sulphate, and this is attributed to the formation of a complex anion, just as is the case when ferric ions are present (compare Küster and Thiel, *Abstr.*, 1899, ii, 247; 1900, ii, 242). Sulphuric acid can, however, be accurately estimated in presence of zinc by carefully adding ammonia to the solution until the zinc is precipitated as hydroxide and the solution just shows an alkaline reaction towards phenolphthalein. Barium chloride is added, and the zinc hydroxide then dissolved in a very slight excess of hydrochloric acid; the quantity of acid added should be just sufficient to cause the solution to become red when methyl-orange is added. J. McC.

Titration of Sulphuric Acid with Benzidine Hydrochloride. WOLF JOHANNES MÜLLER (*Zeit. angew. Chem.*, 1903, 16, 653—655).—A criticism of the improved volumetric process proposed by Raschig (this vol., ii, 572). Owing to the serious loss caused by the solubility of the precipitate in the water used for washing and the difficulty of noticing the end point of the titration, the author prefers his original process (*Abstr.*, 1902, ii, 425). L. DE K.

Estimation of Sulphuric Acid by means of Benzidine. F. RASCHIG (*Zeit. angew. Chem.*, 1903, 16, 818—823).—A reply to Müller (see preceding abstract) and some further remarks on the process (this vol., ii, 425). The loss due to the solubility of benzidine sulphate in a large quantity of wash-water is too great to be neglected, but if only a moderate amount (say 5 c.c.) is employed this source of error is obviated. It is, however, necessary to use the filter pump and to drain every trace of mother liquor from the precipitate. The titration presents no difficulties whatever. As the precipitate is somewhat soluble in dilute hydrochloric acid, it is as well first to neutralise the solution before pouring this into the reagent.

Solutions of ferric sulphate must be first reduced to the ferrous state, and this may be conveniently effected by boiling with a solution of hydrazine chloride and carefully avoiding an excess of this reagent.

The author gives an improved plan for the preparation of the reagent; 40 grams of benzidine are triturated with 40 c.c. of water, the mixture diluted with 750 c.c. of water, and introduced into a litre flask along with 50 c.c. of strong hydrochloric acid, the whole being then diluted to 1 litre. The clear liquid should be diluted to 20 volumes before use, 300 c.c. of this reagent being sufficient for 0.1 gram of sulphuric acid; the mixture should be allowed to remain undisturbed for a few hours. L. DE K.

Estimation of Phosphorus Dissolved in Oil. WALTHER STRAUB (*Arch. Pharm.*, 1903, 241, 335—340).—Ten c.c. of a 0.1 per cent. solution of phosphorus in olive oil was shaken with 25 c.c. of a

1 per cent. solution of crystallised copper sulphate; at first, a dark brown emulsion is formed, containing copper phosphide; after 4—5 hours' shaking, this colour has disappeared, and the solution separates into two layers when allowed to remain at rest. The aqueous layer contains all the phosphorus as copper phosphate; the phosphate is estimated by precipitating it with molybdic acid, and eventually weighing it as magnesium pyrophosphate. The results are accurate.

C. F. B.

Iodometry of Phosphorus. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 321—326).—0.02—0.04 gram of yellow phosphorus is allowed to remain for 24 hours in a stoppered bottle with 50—100 c.c. of *N*/10 iodine solution, 3—5 grams of sodium potassium tartrate, and about 5 c.c. of purified carbon disulphide, the whole being shaken at intervals; the excess of iodine is then titrated with *N*/10 thio-sulphate solution, with or without the addition of starch as an indicator; 1 c.c. of the iodine solution = 0.00062 gram of phosphorus. The result is as accurate as the error of weighing permits. If arsenic is present, it may be estimated by allowing 0.1 gram of the sample to remain for 26 hours with 3 grams each of iodine, potassium iodide, and sodium hydrogen carbonate, 50 c.c. of water, and 10 c.c. of carbon disulphide; the solution is then acidified with dilute sulphuric acid and heated for $\frac{1}{2}$ hour in order that the arsenic acid may be reduced by the hydriodic acid; the last traces of iodine are removed with sulphurous acid, the excess of this boiled off, excess of sodium hydrogen carbonate added, and the arsenite now present titrated with *N*/100 iodine solution.

Red phosphorus may be estimated in the same way, but sodium hydrogen carbonate must be used instead of the tartrate, and the digestion should be prolonged to $1\frac{1}{4}$ days.

C. F. B.

Detection of Phosphorus. AUGUST FISCHER (*Pflüger's Archiv*, 1900, 97, 578—605).—This is a research undertaken from the medico-legal standpoint. It is pointed out that the Hilger-Nattermann modification of Mitscherlich's method is often inapplicable, for it is prevented by the presence of many medicinal reagents or antidotes administered. A list of these is given with their influence in each case. Special attention is paid to turpentine, which enters into combination with a part of the phosphorus; the compound, however, is not a single one, but a mixture of complex turpentine-phosphorus acids. The modification of the phosphorus tests suggested consists mainly in examining the distillate by the Dussard-Blondlot method. The liver is generally stated to be the organ where most phosphorus accumulates; the brain and spinal cord appear to be still more important; examination of the urine or muscles is useless. The reaction is not given by any of the normal phosphorised constituents of brain, even when putrid, or of potatoes.

W. D. H.

The Phosphomolybdate Reaction. C. REICHARD (*Chem. Zeit.* 1903, 27, 833—835).—A lengthy paper, unsuitable for abstraction, dealing with the action of the ammonium molybdate reagent on phos-

phoric acid. To ensure complete precipitation of very minute quantities of phosphoric acid, the ratio of ammoniummolybdate to phosphoric acid should be approximately 200 : 1. Free hydrochloric acid should first be neutralised with ammonia. Tartaric acid, and particularly citric and oxalic acids, retard or prevent the precipitation, although they do not redissolve the yellow phosphomolybdate when already formed.

L. DE K.

Estimation of Available Phosphoric Acid and Potash in Soils. HERBERT H. COUSINS and H. S. HAMMOND (*Analyst*, 1903, 28, 238—240).—In dealing with certain Jamaican soils abnormally rich in calcium carbonate, the authors found it necessary to follow Hilgard's practice of neutralising the carbonates in the soil before subjecting it to the solvent action of the standard citric acid solution. With these soils, Dyer's method (compare *Trans.*, 1894, 65, 115) gave misleading results. In two cases, however, the carbon dioxide had an additional solvent action as regards the potash.

W. P. S.

Quantitative Estimation of Phosphates in Stomach Contents. GEORGE H. A. CLOWES (*Amer. J. Pharm.*, 1903, 75, 325—330).—When phosphoric acid is titrated with normal sodium hydroxide solution, using alizarin as indicator, neutrality is indicated by the formation of sodium dihydrogen phosphate; with phenolphthalein as indicator, disodium hydrogen phosphate is produced, whilst in presence of excess of barium chloride and of sodium hydroxide, the excess of the latter being titrated in presence of phenolphthalein, neutrality is indicated with the formation of trisodium phosphate. Other indicators, including dimethylaminoazobenzene, give less definite end points, so that the usual practice of regarding the difference between two titrations, in presence of alizarin and dimethylaminoazobenzene respectively, as due to acid phosphates and organic acids, and that between two titrations, using respectively alizarin and phenolphthalein, as due to hydrochloric acid is inaccurate. The following process is proposed: at least 20 c.c. of the contents are evaporated to dryness and the residue gently incinerated. The ash is dissolved in dilute sulphuric acid and the solution made up to 25 c.c. Of this liquid, 10 c.c. are exactly neutralised with sodium hydroxide solution, using phenolphthalein as indicator; alizarin is then added and the liquid made neutral to this indicator by titration with decinormal sulphuric acid. This reading is the equivalent of one of the acid functions of the phosphoric acid present. To another 10 c.c. of the liquid, neutralised as before, a slight excess of barium chloride is added, followed by a definite excess of sodium hydroxide. The mixture is boiled for one minute, slightly cooled, and titrated with normal sulphuric acid in presence of phenolphthalein. The difference between the amounts of acid and alkali added is the equivalent of another acid function of the phosphoric acid present and should be identical with the previous reading.

T. A. H.

Rapid Estimation of Phosphorus in Steel. GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1903, 25, 772—773).—One gram of steel is

dissolved in 50 c.c. of nitric acid of sp. gr. 1.135, the solution is boiled with a little solid permanganate, and the excess of this reagent destroyed by cautious addition of ferrous sulphate. The cold solution is shaken in an Erlenmeyer flask with 10 c.c. of ammonia and 50 c.c. of molybdate solution, the liquid with the precipitate being then transferred to a test-tube which, after half an hour, is rotated in a centrifugal machine. The supernatant liquid may then be completely poured off without any loss of precipitate, and the tube is now filled with water, shaken, and again subjected to centrifugal action. After decanting the washing liquid, the precipitate is titrated according to Handy's directions with standard alkali and acid. L. DE K.

Estimation of Sulphur in Iron or Steel; Volumetric Estimation of Arsenic. A. KLEINE (*Chem. Zeit.*, 1903, 27, 729).—*Estimation of Sulphur in Iron or Steel.*—Five grams of iron or 10 grams of steel are heated with 100 c.c. of water and 70 c.c. of hydrochloric acid in a flask provided with a special cooling arrangement, and connected with an absorption vessel constructed so as to prevent any back flow of liquid into the distilling flask. A figure of the apparatus is given in the original paper. The gases evolved are passed through 50 c.c. of an ammoniacal solution of cadmium chloride and the precipitated cadmium sulphide is collected and then titrated with standard iodine in the presence of dilute hydrochloric acid with starch as indicator.

Volumetric Estimation of Arsenic.—Arsenic trisulphide may be estimated by dissolving it in ammonia and adding an ammoniacal solution of cadmium chloride. The cadmium sulphide thus obtained is then titrated as described in the preceding estimation. L. DE K.

Purification of Hydrogen Sulphide to be used in the Detection of Arsenic. ARMAND GAUTIER (*Bull. Soc. chim.*, 1903, [iii], 29, 867—868).—Hydrogen sulphide, prepared in the usual way from ferrous sulphide, contains hydrogen arsenide, which is not completely removed by washing the gas with water or nitric acid. The author proposes to eliminate this impurity by washing the gas with water, passing it through a short tower containing moistened pumice stone, then along a tube containing small fragments of glass maintained at a low red heat, then through a serpentine wash-bottle containing barium sulphide solution, and finally through cotton-wool.

T. A. H.

Estimation of Carbonic Acid in Drinking Water. FREDERIC B. FORBES and GILBERT H. PRATT (*J. Amer. Chem. Soc.*, 1903, 25, 742—756).—The amount of carbon dioxide present in drinking water in the free state and in combination as hydrogen carbonate are separately estimated, and comparative results are given of determinations made by the direct method, the method of Pettenkofer (slightly modified by the authors), and the Lunge-Trillich or Seyler method.

The authors conclude that the Seyler method (titration of free carbon dioxide with $N/50$ sodium carbonate and phenolphthalein, &c.) is the most convenient process for technical purposes. L. DE K.

Estimation of Potassium and Sodium in the Urine. WILLIAM H. HURLEY and KENNEDY J. P. ORTON (*J. Physiol.*, 1903, 30, 10—14).—The chlorides are converted into sulphates before the organic matter is burnt off; but instead of evaporating the urine with ammonium sulphate and then igniting, it is more effectual to add a small amount of pyrosulphuric acid to the residue left after evaporating the urine to dryness; a rapid oxidation of the organic matter then takes place. It is then necessary to remove all magnesium from the chlorides which are obtained by the addition of hydrochloric acid. Another method given is a slight modification of Neubauer and Vogel's process, but here a very small amount of magnesium chloride and possibly a trace of calcium chloride are left in the mixture; in spite of this, a small loss always occurs. These methods may be employed also in the analysis of faeces, lymph, blood, meat, &c. W. D. H.

Volumetric Estimation of Calcium and Magnesium in Water from Salt Marshes. ALEXANDRE D'ANSELME (*Bull. Soc. chim.*, 1903, [iii], 29, 734—735).—Four parts of sodium carbonate and one part of sodium hydroxide are dissolved in water and the solution is diluted so as to correspond with *N*-sulphuric acid, using methyl-orange as indicator. One hundred c.c. of the brine are mixed with 10 c.c. of the alkali, heated, and filtered, and the filtrate is titrated with *N*-sulphuric acid. The difference between 10 and the number of c.c. of acid used represents the total calcium and magnesium oxides.

Another experiment is then made without heating in the presence of 100 c.c. of a 10 per cent. solution of ammonium chloride, and the difference will this time represent the calcium oxide only. In practice, the calcium is calculated to sulphate and the magnesium to chloride. L. DE K.

Iodometric Estimation of Zinc with Potassium Ferrocyanide. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 331—335).—The ultimate action of excess of potassium ferrocyanide on a zinc salt, for example, zinc sulphate, corresponds with the equation $2K_4Fe(CN)_6 + 3ZnSO_4 = 3K_2SO_4 + 2K_2Zn_3[Fe(CN)_6]_2$. For the estimation, 10 c.c. of the zinc solution, containing about 0.12 gram of zinc, are mixed with 20 c.c. of *N*/10 potassium ferrocyanide solution, diluted with a little water, and allowed to remain for half an hour; 20 c.c. of *N*/10 iodine solution are then added, the whole allowed to remain for 1 hour, and the excess of iodine then titrated with *N*/10 thiosulphate solution using starch as indicator; 1 c.c. of the *N*/10 solution = 0.00981 gram of zinc. In two test experiments, the error was -0.4 and +0.1 per cent. of the total quantity respectively.

In the case of manganese, cobalt, copper and nickel the method did not lead to satisfactory results. C. F. B.

Volumetric Determination of Mercury and of Hydrogen Cyanide. LAUNCELOT W. ANDREWS (*Amer. Chem. J.*, 1903, 30, 187—193).—To estimate hydrogen cyanide, decinormal hydrochloric acid is added to its solution until the coloration due to the indicator, *p*-nitrophenol, has almost disappeared. An excess of mercuric chloride

solution is then added, and, after one hour at the ordinary temperature, the liquid is titrated with decinormal potassium hydroxide solution.

For the estimation of mercury by this method, the mercury must be in the form of the chloride and organic acids must be absent. The solution is exactly neutralised and an excess of the standard "neutral" solution of hydrogen cyanide is added and the liberated hydrochloric acid determined by means of standard alkali. A. McK.

Iodometric Estimation of Mercuric Cyanide. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 328—330).—Mercuric cyanide reacts with iodine according to the equation $\text{Hg}(\text{CN})_2 + 2\text{I}_2 + 2\text{KI} = \text{K}_2\text{HgI}_4 + 2\text{CNI}$, but the yellow colour of the cyanogen iodide obscures the end point. This difficulty can be obviated by making two titrations, in which respectively the iodine solution is added to the cyanide solution, and *vice versa*; the two results differ by about 4 per cent., but the mean of them is correct.

A solution of the mercuric cyanide is prepared of about 1 per cent. strength. In one experiment, 10 c.c. of this solution is mixed with about $\frac{1}{2}$ gram of sodium hydrogen carbonate and titrated with *N*/10 iodine solution until a distinct yellow colour has appeared. An amount of the iodine solution about equal to that just used is taken in a second experiment, mixed with carbonate as before, and titrated with the cyanide solution until a feeble yellow tint is obtained. The mean of the two results is taken as correct; 1 c.c. of *N*/10 iodine = 0.0063095 gram $\text{Hg}(\text{CN})_2$. C. F. B.

Detection of Mercury in Urine. M. OPPENHEIM (*Zeit. anal. Chem.*, 1903, 42, 431—433).—The author, in testifying to the simplicity, sensitiveness, and trustworthiness of Jolles's method (*Abstr.*, 1900, ii, 576; this vol., ii, 44) for the qualitative detection of mercury in urine, recommends that the gilt platinum foil should before use be heated for 15 minutes with dilute nitric acid, and that concentrated acid should be employed in dissolving the mercury for the colorimetric test. M. J. S.

A Higher Oxide of Cobalt; Volumetric Estimation of Cobalt. ROBERT L. TAYLOR (*Mem. Manchester Phil. Soc.*, 1903, [v], 12, 1—10).—The cobalt precipitate, obtained by treating a neutral solution of a cobaltous salt with calcium carbonate and bromine water (*Abstr.*, 1902, ii, 476), has been investigated by the author and found to have a composition agreeing with the formula Co_7O_{11} or Co_9O_{14} . On this fact, a method for the titration of cobalt in the presence of nickel has been founded. The presence of other metals, even zinc, seriously interferes with the estimation.

The neutralised solution containing from 0.07—0.1 gram of cobalt is diluted to 150 c.c., a little milk of precipitated calcium carbonate is added, and then an excess of bromine water. After 10 minutes, the precipitate is collected, well washed, and put back into the beaker. A solution of potassium iodide is added, followed by a sufficiency of dilute hydrochloric acid. The liquid is then suitably diluted and the liberated iodine titrated as usual with *N*/10 sodium thiosulphate, 1 c.c.

of which = 0.005244 gram of metallic cobalt. Nickel is also precipitated in the presence of calcium carbonate and bromine if the temperature is raised to 80—100°, but the oxide is not sufficiently definite for the purpose of analysis.

L. DE K.

Estimation of Manganese as Sulphide. H. RAAB and L. WESSELY (*Zeit. anal. Chem.*, 1903, 42, 433—434).—According to the temperature and other conditions of precipitation, manganese may be thrown down either as the flesh-coloured hydrated sulphide, or as the dense green anhydrous sulphide. In the former case, precipitation is often imperfect and filtration difficult. In the latter case, the obstinate adherence of the precipitate to the filter paper entails difficulties in the ignition. By precipitating below the boiling point, then converting the hydrated into the anhydrous sulphide by heating with excess of ammonia, and filling the filter once with alcohol after the precipitate has been thoroughly washed with ammonium sulphide, all these difficulties are obviated; the dry precipitate can be detached completely from the paper, and generally shows a constant weight after a single ignition.

M. J. S.

Titration of Antimony in Crude Lead. H. NISSENSON and PH. SIEDLER (*Chem. Zeit.*, 1903, 27, 749—752).—One gram of the powdered sample is heated with 20 c.c. of a saturated solution of bromine in hydrochloric acid until dissolved, the excess of bromine being then boiled off. The antimony is next reduced to the antimonious state by means of solid sodium sulphite, the excess of sulphur dioxide produced is expelled by boiling, 20 c.c. of dilute hydrochloric acid are then added, the liquid again heated to boiling, and titrated whilst hot with a standard solution of sodium bromate, using methyl-orange or, preferably, indigo as indicator. It is advisable not to add the indicator until the antimony is nearly all oxidised, so that, in the case of unknown alloys, at least two estimations are necessary.

The process is not affected by the other metallic impurities contained in hard lead.

L. DE K.

Iodometric Estimation of Gold in Dilute Solution. RALPH N. MAXSON (*Amer. J. Sci.*, 1903, 16, 155—160).—The process devised by Gooch and Morley (*Abstr.*, 1900, ii, 110) for the titration of auric chloride by means of potassium iodide and sodium thio-sulphate has been adversely criticised by Rupp (*Abstr.*, 1900, ii, 479), who proposed, instead, a method based on the reduction of auric chloride with excess of arsenious acid, followed by iodometric titration.

The author finds Rupp's process quite untrustworthy when dealing with very minute quantities of gold, and prefers the original method of Gooch and Morley.

L. DE K.

Estimation of Organic Matter in Waters; especially those containing Chlorides and Bromides. C. LE-NORMAND (*Bull. Soc. chim.*, 1903, [iii], 29, 810—814).—A mixture of 100 c.c. of the water under examination with 10 c.c. of a solution of potassium permanganate, containing 0.395 gram of the salt per litre, and 10 c.c. of a

saturated solution of sodium hydrogen carbonate is boiled for 10 minutes in a glass vessel. When cold, the volume is made up to 100 c.c. and the amount of unchanged permanganate determined by ascertaining what quantity of distilled water must be added to the liquid, decanted from the precipitate of manganese dioxide formed, in order to produce a tint identical with that of a solution of permanganate containing 0.0395 gram of this salt per litre. Using the Duboscq colorimeter, this quantity is equal to $H_1 - H$, where H_1 and H are the respective heights of the liquids in the two test glasses when the tints are identical, whence the quantity of permanganate reduced is equivalent to $0.00395 (H_1 - H)/H_1$ or, since 0.00395 of permanganate is equivalent to 0.001 gram of oxygen, to $(H_1 - H)/H_1$ milligrams of oxygen. The results obtained in a series of experiments made, (a) with sea-water, and (b) with sea-water to which known quantities of peptone had been added, showed that the method gives constant results and is sufficiently sensitive for general application. The procedure described above is intended for use with sea-water; in the case of fresh water, it is necessary to add to the sample 1 c.c. of a saturated solution of magnesium sulphate, whereby a precipitate of hydrated magnesium carbonate is formed on ebullition, which facilitates the clearing of the liquid from manganese dioxide. Where the quantity of organic matter present is small, the comparison is more readily made with the aid of the green glass provided with the Duboscq colorimeter, and the comparison of tints is also facilitated by the use of a standard solution prepared by boiling distilled water with the permanganate, sodium hydrogen carbonate, and magnesium sulphate solutions in the manner prescribed for the water under examination.

T. A. H.

Analysis of Bordeaux Oil of Turpentine. MAURICE VÈZES (*Bull. Soc. chim.*, 1903, [iii], 29, 896—901).—When a given quantity of Bordeaux oil of turpentine is divided into 5 equal portions by distillation, the first four portions being distillates successively collected and the fifth the residual undistilled liquid, there is a fairly constant difference between the refractive index of each of the extreme fractions (1 and 5) and that of the middle fraction (3). These two differences are modified either singly or simultaneously by the presence of foreign substances: thus the difference $n_3 - n_1$ is scarcely affected by the presence of resin or resin oil, whilst the difference $n_5 - n_3$ is considerably modified under these conditions. The total quantity per cent. X of these constituents may be found from the relation $\Delta = 0.0032 + 0.0037 X$, where $\Delta = n_5 - n_3$, whilst the quantity of resin present may be ascertained by titration of 10 c.c. of the oil dissolved in 10 c.c. of alcohol, with standard alkali. In rectified Bordeaux oil of turpentine, the value of X should not be more than 2.5 per cent., and of this not more than 1 per cent. should be resin. The other possible adulterants of turpentine oil usually affect the difference $n_3 - n_1$, and the quantity per cent. (P) of such an adulterant may be ascertained from the relationship $\delta - 0.0007/x = P$, where δ is the observed difference $n_3 - n_1$, and x is a factor dependent on the nature of the sophistication. The following values for x have been ascertained: petroleum, 0.0002; "white

spirit," 0.008; light petroleum, 0.0025; "benzine," -0.0009; and carbon disulphide, -0.0046. For unadulterated turpentine oil, the value of δ lies between 0 and 0.001, whilst Δ is not greater than 0.0125, and the initial boiling point is not lower than 150°.

T. A. H.

Estimation of Chloroform by Densimetry. AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1903, vi; *J. Physiol.*, 30). **Estimation of Ether by Densimetry** (*ibid.*, vii). **Densimetric Estimation of the Pulmonary Absorption of Ether Vapour** (*ibid.*, xii—xv).—The method consists in weighing a 260 c.c. flask full of air, and then full of the mixture to be examined; units per cent. of chloroform vapour are indicated by centigram increments of weight. In the case of ether vapour, the unit per cent. is half this value. Formulæ for corrections for temperature and pressure are given. If such estimations are made in the mixture given to an animal, and in the air it expires, the actual amount of the anæsthetic retained in the body with respiration of given volume for a given time can be determined, and also an estimate can be made of the rapidity with which the anæsthetic is exhaled after its administration has been suspended. W. D. H.

Iodometric Estimation of Chloral Hydrate. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 326—328).—A 1 per cent. solution of the chloral hydrate is prepared, and 10 c.c. of this allowed to remain for 5—10 minutes in a stoppered bottle with a mixture of 25 c.c. of *N*/10 iodine solution with 2.5 c.c. of *N* potassium hydroxide solution. The solution is then diluted with 50 c.c. of water, 5 c.c. of officinal hydrochloric acid are added, and the iodine liberated is titrated with *N*/10 thiosulphate solution. The amount of the last used should vary from 12.9 to 13.5 c.c., corresponding with a percentage of 100 to 95 of chloral hydrate. The reaction is $\text{CCl}_3 \cdot \text{CHO} + \text{H}_2\text{O} + 2\text{I} + 2\text{KOH} = 2\text{KI} + 2\text{H}_2\text{O} + \text{CO}_2 + \text{CHCl}_3$.

C. F. B.

A Source of Error still remaining in Optical Sugar Analysis. FERDINAND G. WIECHMANN (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 568, 498—509).—As is well known, the volume occupied by the precipitate formed when basic lead acetate is added as a clarifier to a solution of a raw sugar introduces an error into the polarimetric reading. Two methods have been suggested for eliminating this error: (1) that of Scheibler, in which two separate normal weights of the sugar are dissolved in water and made up, in one case, to 100 c.c., and in the other to 200 c.c., the same volume of lead acetate solution being added to each solution. The true polarisation is then calculated from the values for the two solutions. This method, which assumes that the volume of the precipitated matter is independent of the dilution of the liquid, is found to give discordant results, especially when raw colonial sugars are treated. (2) Sachs's method, in which the influence of the precipitate is determined by washing it free from sugar, adding it to a 100 c.c. flask containing the half-normal weight of pure sugar, making the solution up to the volume, filtering, and taking the polarimeter reading.

The author has made use of both these methods in the examination of various sugars, and he finds that the volumes of precipitate formed with sugars of different origin, but giving approximately the same reading in the polarimeter, are widely different. For a number of raw cane-sugars, the volume of precipitate varied from 0.05 to 0.71 c.c., the specific gravities (determined in benzine) ranging from 1.65 to 4.38. The most voluminous precipitates are not always obtained with the sugars of lowest value.

The addition of a few drops of acetic acid to the sugar solution, after lead acetate, causes a difference in the polarisation value in only a few cases, and this difference was never greater than 0.1 division Ventzke.

The errors introduced into the polarimeter reading by different temperatures of working are much smaller than the above, and in ordinary cases are always less than 0.1 division Ventzke.

The author suggests that the magnitude of the error introduced by the lead precipitate should be determined under different circumstances and due allowance made.

T. H. P.

Furfuraldehyde and some Aromatic Aldehydes as a Test for Fusel Oil or *iso* Amyl Alcohol in Spirits of Wine. ABRAM KOMAROWSKY (*Chem. Zeit.*, 1903, 27, 807—808).—Ten c.c. of the spirit to be tested are mixed with 1 c.c. of alcoholic solution of furfuraldehyde (1:1000) and 15 c.c. of sulphuric acid are added. According to the amount of *iso* amyl alcohol present, the liquid assumes a more or less intensive rose colour. Instead of furfuraldehyde, 25—30 drops of an alcoholic solution of salicylaldehyde (1:100) may be used, followed by 25 c.c. of sulphuric acid, or 1 c.c. of a 2 per cent. alcoholic solution of *p*-hydroxybenzaldehyde and 20 c.c. of sulphuric acid may be added. Benzaldehyde also gives red colorations.

L. DE K.

Gasometric Estimation of Formic Acid and its Salts. M. WEGNER (*Zeit. anal. Chem.*, 1903, 42, 427—431).—By heating with strong sulphuric acid, formic acid is quantitatively resolved into water and carbon monoxide. The decomposition is carried out in a flask through which carbon dioxide is passed to expel air, and, since a small portion of the formic acid distils over undecomposed, the gases are passed through a second flask containing sulphuric acid at 180°. The formate (0.1 gram in 2 c.c. of solution) having been introduced into the first flask, 25—30 c.c. of concentrated sulphuric acid are slowly admitted from a dropping funnel, and when the evolution of gas ceases, this mixture is also heated at 180°. The carbon monoxide is finally driven over by carbon dioxide into a measuring tube containing potassium hydroxide solution.

M. J. S.

Detection and Estimation of Mineral Acid in Acetic Acid and Vinegar. PHILIP SCHIDROWITZ (*Analyst*, 1903, 28, 233—237).—The addition of sufficient ethyl alcohol to a solution of acetic acid prevents the reaction of the latter on methyl-orange, and further, a solution of acetic acid coloured pink with methyl-orange solution turns yellow on the addition of alcohol provided that no mineral acid

is present. The best results are obtained by adding an equal volume of alcohol to the solution to be titrated and afterwards 1 c.c. of alcohol for every 3 c.c. of $N/10$ alkali run in. The method is trustworthy within a limit of 0.01 per cent. In the case of vinegar, it is better to use methyl-orange paper instead of adding the indicator in solution. Animal charcoal cannot be employed to decolorise the vinegar, as it retains a considerable portion of the mineral acid which may be present.

W. P. S.

Estimation of Succinic Acid in Wine and some remarks on the Estimation of Malic and Lactic Acids in Wine. RUDOLF KUNZ (*Zeit. Nahr. Genussm.*, 1903, 6, 721–729).—One hundred and fifty c.c. of the wine are evaporated to 100 c.c., treated with 4 grams of barium hydroxide and 3 c.c. of barium chloride solution (10 per cent.), and then made up to 150 c.c. After filtration, 100 c.c. are boiled in a reflux apparatus for 10 minutes, treated with carbon dioxide, and then evaporated to a viscid syrup. To the latter, 20 c.c. of water and 80 c.c. of alcohol (95 per cent. by volume) are added, and after 2 hours the precipitate is collected on a filter, washed with alcohol, then removed from the filter, and decomposed with dilute sulphuric acid. The solution is heated, and potassium permanganate solution is cautiously added until a permanent pink coloration is produced. The excess of permanganate is destroyed by the addition of ferrous sulphate and the whole solution evaporated to a volume of 50 c.c. It is then extracted with ether for 16 hours in a Schacherl's apparatus. The ether extract is dissolved in a little hot water, filtered, evaporated to dryness, and the succinic acid so obtained titrated with $N/10$ sodium hydroxide, using phenolphthalein as indicator. As the extracted succinic acid may contain traces of sulphuric acid and acetic acid, it is preferable to add a known volume of $N/10$ silver solution to the neutralised extract and titrate back the excess of silver by Volhard's method, after removing the insoluble silver salts by filtration. One c.c. of $N/10$ silver solution = 0.0059 gram of succinic acid. The amount of the latter found in wine varied, according to the analyses given, from 0.060 to 0.115 per cent.

A method is given for estimating malic acid in wine and consists in treating 100 c.c. of the latter with barium hydroxide and alcohol, mixing the precipitate formed with sodium hydroxide, and heating the mixture to 120–130°. The residue is dissolved in dilute hydrochloric acid, the solution rendered alkaline with calcium hydroxide, and filtered. A portion of the filtrate is then extracted with ether, when the fumaric acid resulting from the action of the sodium hydroxide on the malic acid is obtained in the ethereal solution together with the succinic acid in the wine.

With regard to the estimation of lactic acid in wine, the author finds that about 3.5 per cent. of the lactic acid distils over with the volatile acids (compare Abstr., 1903, ii, 189).

W. P. S.

Gasometric Estimation of "Cream of Tartar" and of Potassium. DE SAVORITA (*J. Pharm. Chim.*, 1903, [vi], 18, 61–66).—Twenty-five grams of the finely powdered "cream of tartar" are

mixed with 5 grams of boric acid and added to 500 c.c. of water. The mixture is boiled for five minutes, cooled, and made up to 1 litre. To 20 c.c. of this liquid, contained in a calcimeter, a slight excess of potassium hydrogen carbonate is added, and the amount (N_1) of carbon dioxide liberated, is determined. The quantity (N) of carbon dioxide liberated by 20 c.c. of a solution of pure tartaric acid, containing 10 grams of the acid per litre, is then determined under the same conditions. The amount of potassium hydrogen tartrate contained in the material is equal to $100N_1/N$. The quantity of boric acid employed should not exceed that required to convert the potassium hydrogen tartrate of the "cream of tartar" into the "boron emetic."

The solubility of potassium hydrogen tartrate in a solution of boric acid may also be utilised indirectly for the estimation of potassium. When a neutral potassium salt is dissolved in saturated solution of potassium hydrogen tartrate and excess of sodium hydrogen tartrate is then added, the whole of the potassium is precipitated as potassium hydrogen tartrate at the end of a few hours. The amount of this precipitate may then be ascertained by dissolving it in a solution of boric acid and estimating in a known fraction of the solution the amount of potassium hydrogen tartrate, by the process outlined in the preceding paragraph. A detailed account is given in the original of a process based on this principle which is sufficiently accurate for many industrial and agricultural purposes. T. A. H.

New Method of Fat Estimation. C. LEHMANN (*Pflüger's Archiv*, 1903, 97, 419—420). W. VÖLTZ (*ibid.*, 606—633).—The tissue or food material must be finely divided, and although in many cases Soxhlet's method gives good results, in many others it does not, and Dormeyer's method of preliminary digestion is not regarded as trustworthy, as by this means fat is liberated from such substances as proteid, and so the result obtained is too high. The best method consists in extracting with ether, renewed three or four times, while the tissue all the time (12—24 hours) is being ground in a mill worked by a motor.

W. D. H.

Estimation of Fat in Animal Fluids. MUNEO KUMAGAWA and KENZO SUTO (*Beitr. chem. Physiol. Path.*, 1903, 4, 185—191).—Dormeyer's method for the extraction of fat from muscle is also recommended for estimation of fat in animal fluids (milk, blood, &c.). The process consists in subjecting the material to a brief gastric digestion before extracting with ether. The method of preparing the pepsin-hydrochloric acid used for this purpose is described, and also a new ether extracting apparatus is described and figured. The analytical figures given in reference to milk show a larger yield of fat by this method as compared with other methods. Further details concerning results in blood serum and serous effusions are promised.

W. D. H.

Evaluation of Bees' Wax. RAGNAR BERG (*Chem. Zeit.*, 1903, 27, 752—756).—A table giving the result of the investigation of a number of samples of 38 commercial varieties of bees' wax, also of two samples of commercial stearin, one sample of Japan wax, and one

of carnauba wax (compare Abstr., 1884, 1280). The data include the maximum, minimum, and mean values of the acid number, ester number, saponification number, Büchner number, iodine number, specific refraction (taken at 84° but reduced to 40°), and the melting point. The saponification number is the sum of the ester and acid number; the ratio of these constants is also tabulated. The melting points and the specific refractions of several varieties of paraffin wax are also recorded. A full description is also given of the various processes employed.

L. DE K.

Examination of Linseed Oil. B. SJOLLEMA (*Zeit. Nahr. Genussm.*, 1903, 6, 631—637).—Pure linseed oil remains perfectly liquid when cooled to 0° , thus differing from most other oils. The presence of free fatty acids, however, causes crystallisation to take place. Some linseed oils (for example, North Russian), which remain clear at -14° , may be adulterated with several per cent. of cotton oil and still remain clear at 0° . The author considers that the refractive index more plainly indicates admixture than does the iodine value. The refractive index, however, is influenced by the following conditions: (1) it is greatly lowered by the presence of free fatty acids, each 10 per cent. of the latter depressing the reading by about 1.5 scale-degrees. (2) Each degree of temperature above 15° decreases the reading by 0.6 scale-degrees, and correspondingly increases it below 15° . (3) Oxidation increases the refractive index.

Mineral or rosin oils have higher refractive indices than linseed oil, most other oils giving lower readings. The refractive indices of linseed oils from various countries are given, the numbers varying between 87.0 and 91.5 at 15° .

W. P. S.

Influence of Atmospheric Oxidation on the Composition and Analytical Constants of Oils. H. C. SHERMAN and M. J. FALK (*J. Amer. Chem. Soc.*, 1903, 25, 711—716. Compare Abstr., 1901, ii, 430; 1902, ii, 435).—The authors submit a table showing the great change oils undergo when exposed to the air in uncorked bottles. If the original specific gravity of the sample of oil is known, the original Hübl number may be calculated with reasonable accuracy by multiplying the figure representing the percentage increase in specific gravity by 7.46 and adding the result to the Hübl number actually obtained. This process is only trustworthy for non-drying and semi-drying oils, and not for drying oils or fish oils. Conversely, the original specific gravity may be calculated if the original Hübl number is known.

L. DE K.

Occurrence of Salicylic Acid in Wines, also in Grapes and other Fruits. HUGO MASTBAUM (*Chem. Zeit.*, 1903, 27, 829—833).—It is no longer doubted that most natural wines contain traces of a crystalline substance which gives the reactions of salicylic acid, but it should be remembered that this product has not as yet been isolated in sufficient quantity to submit it to organic analysis and other crucial tests. In the case of grapes, this substance occurs chiefly in the stalks; in the case of strawberries, in the stalks and calyx. It

is still somewhat doubtful whether raspberries contain salicylic acid, and up to the present this acid has not been found in gooseberries, blackberries, red currants, bilberries, cranberries, cherries, plums, apples, pears, and quince. L. DE K.

Estimation of Pyridine in Aqueous Solution. MAURICE FRANÇOIS (*Compt. rend.*, 1903, 137, 324—326).—Pyridine cannot be estimated by titration with acid, nor is the precipitation of the periodide (Prescott and Trowbridge, *Abstr.*, 1896, i, 186) sufficiently complete or the composition of the deposit sufficiently definite to allow of the estimation on this basis. The estimation can be carried out by precipitating with auric chloride. The pyridine should be present in solution as hydrochloride; a little hydrochloric acid is added and then an excess of auric chloride. The liquid is evaporated to dryness on the water-bath and the residue is washed with dry ether free from aldehyde. The washing is continued until the ether does not become yellow. The washings are filtered and the insoluble residue transferred to a small weighed crucible. Any precipitate which adheres to the vessel and is not loosened by the ether is dissolved in a little water and the solution added to the weighed crucible; the water is carefully evaporated on the water-bath and the filter is then incinerated and the ash added to the pyridine aurichloride. The substance is ignited and the residual gold weighed. 196.6 parts of gold correspond with 79 parts of pyridine, since the formula of the precipitate is $C_5H_5N, HAuCl_4$.

Results are given which show that the method is accurate.

J. McC.

Quantitative Separation of Strychnine from Quinine. EDWARD FRANK HARRISON and D. GAIR (*Pharm. J.*, 1903, [iv], 17, 165).—A quantity of the mixed alkaloids containing from 0.05 to 0.1 gram of strychnine is added to 60 c.c. of water and dissolved by the addition of a little dilute sulphuric acid. To this liquid, ammonia solution is added as long as the precipitate first formed re-dissolves, then 15 grams of sodium potassium tartrate and finally ammonia solution is added until the liquid is just acid to litmus. The mixture is warmed for 15 minutes on the water-bath, allowed to cool, and the quinine tartrate collected. The precipitate is washed with a solution of 15 grams of sodium potassium tartrate in 45 c.c. of water, slightly acidified with sulphuric acid, and the filtrate, together with the washings, made alkaline with ammonia solution and extracted with chloroform. The solution of strychnine in chloroform is purified by washing once with 10 c.c. of water, to which a few drops of ammonia have been added, and the alkaloid obtained by evaporating the solution to 4 or 5 c.c., adding 10 c.c. of alcohol, evaporating to dryness and washing the residue three times with 1 c.c. of ether. When the quantity of mixed alkaloids taken contains more than 0.1 gram of strychnine, a proportionately larger quantity of sodium potassium tartrate is required to completely precipitate the quinine. The results quoted in the original indicate that strychnine may be satisfactorily estimated by this method in presence of from 10 to 30 times its weight of quinine or quinine sulphate. T. A. H.

General and Physical Chemistry.

Variation of the Index of Refraction of Salt Solutions with the Concentration. B. WALTER (*Ann. Physik*, 1903, [iv], 12, 671—672).—In a recent paper with the above title (*Ann. Physik*, 1903, 11, 593), Wallot has criticised some work of the author's (Abstr., 1890, 202). To these criticisms, the author now replies. J. C. P.

Optical Study of *iso*Nitroso-derivatives. Influence of Negative Radicles. PAUL TH. MULLER and ED. BAUER (*J. Chim. phys.*, 1903, 1, 190—202).—The molecular refraction and dispersion of a number of *isonitroso*-derivatives were determined, Lorenz's formula being used. The results obtained were as follows:

	Ma.			M _γ - Ma.		
	Found.	Calc.	Diff.	Found.	Calc.	Diff.
Acetoxime	20·21	20·27	-0·06	—	—	—
Ethyl α- <i>isonitroso</i> propionate ...	31·50	31·19	+0·31	1·23	0·88	+0·35
α- <i>iso</i> Nitrosopropionic acid	22·45	21·90	+0·55	0·86	0·67	+0·19
<i>iso</i> Nitrosoacetone	21·39	20·39	+1·00	1·19	0·65	+0·54
<i>iso</i> Nitrosomethylacetone	25·93	24·97	+0·96	1·13	0·76	+0·37
Ethyl <i>isonitroso</i> acetoacetate ...	37·37	35·88	+1·49	1·40	1·01	+0·39
Methyl <i>isonitroso</i> malonate	34·09	32·97	+1·12	1·11	0·91	+0·20
<i>iso</i> Nitrosomalonic acid	25·28	23·53	+1·75	1·25	0·70	+0·55
Ethyl <i>isonitroso</i> cynoacetate ...	32·83	31·06	+1·77	1·88	0·86	+1·02
<i>iso</i> Nitrosocynoacetic acid	23·78	21·77	+2·01	—	—	—
<i>iso</i> Nitrosocamphor	49·14	47·98	+1·16	—	—	—

It is seen that the presence of negative radicles causes an increase of both the molecular refraction and dispersion, the values being considerably higher than those calculated additively, this being especially marked for the acetyl group. L. M. J.

Optical Method for Recognition of *pseudo*-Acids. PAUL TH. MULLER and ED. BAUER (*J. Chim. phys.*, 1903, 1, 203—211).—The method has been previously indicated (Abstr., 1902, i, 354), and the authors find that *isonitroso*-propionic, -malonic, and -cyanoacetic acids are true acids, but that the oximido-compounds examined (previous abstract) which owe their acidic character to the influence of negative radicles all behave as *pseudo*-acids. Various formulæ are suggested which may represent the sodium derivatives in these cases. L. M. J.

Spectra of the Metals in the Electric Arc. VI. Spectrum of Molybdenum. BERNHARD HASSELBERG (*K. Svenska Vet.-Akad. Handl.*, 1903, 36, 2. Compare Abstr., 1900, ii, 381).—After careful comparison with the spectra of iron, chromium, cobalt, nickel, manganese, titanium, and vanadium, the author gives a full list of the lines which he regards as characteristic of molybdenum. The relation of this metal to the spectrum of the sun is discussed, and numerous coincidences in the two spectra are detected. The paper is illustrated by a number of photographic reproductions. J. C. P.

Ultra-Violet Absorption Spectra of Ortho-, Meta-, and Para-Isomerides. I. R. MAGINI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 87—95).—Comparison of the absorption spectra of solutions of catechol, resorcinol, and quinol shows that they have in common very sharp bands in the region extending from $\lambda=2900$ to $\lambda=2500$. The ortho- and meta compounds also show the same maximum and minimum of transparency; with quinol, however, it appears to be displaced towards the luminous part of the spectrum. Quinol also differs from its isomerides in exhibiting a peculiar absorption in the extreme ultra-violet, beginning at about $\lambda=2500$. The greatest absorption is shown by quinol and the least by resorcinol.

The three hydroxybenzoic acids have very intense absorption spectra, which, however, exhibit no analogies with each other. In very dilute solutions, the para-compound possesses the strongest absorptive power and the meta-acid the least. The absorption bands of these acids are nearer the visible spectrum than those of the dihydroxy-phenols. The para-acid shows no band in the more refrangible part of the spectrum, the whole of this region being absorbed; on increasing the dilution, the absorption disappears only from the less refrangible portion and does not diminish at both sides, as is usually the case. The few benzene derivatives which possess spectra of this kind, iodobenzene, aniline, and pyridine, show continuous absorption.

T. H. P.

Fluorescence and Chemical Constitution. RICHARD MEYER (*Ber.*, 1903, 36, 2967—2970. Compare Abstr., 1898, ii, 105 and 275).—That fluorescein, which contains the pyrone ring, fluoresces, whereas phenolphthalein, where the pyrone ring is absent, does not, is adduced as evidence of the "fluorophore" nature of the pyrone ring. In a preceding paper (this vol., i, 833), it is shown that phenolphthalein cannot undergo tautomeric change, so that its non-fluorescence agrees with Hewitt's theory (*Proc.*, 1902, 18, 86). Similarly, quinolphthalein, an isomeride of fluorescein, which shows no tendency to undergo tautomeric change and contains no fluorophore, does not fluoresce. The view is advanced that fluorescence is conditioned by the presence of a fluorophore and the possibility of symmetrical tautomeric change as advocated by Hewitt. E. F. A.

Influence of Alkalis on the Speed of Development of Organic Developers. M. L. GUREWITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 498—513).—The author shows that the speed of develop-

ment of catechol or adurol is not influenced by the presence of sodium sulphite.

From experiments made with a number of developers, the following conclusions are drawn. The maximum speed of development is attained in the presence of just sufficient alkali to replace all the hydrogen of the hydroxyl group of the developer by a metal. The alkali of a developer may be replaced by any amine soluble in water. The time of development is approximately inversely proportional to the concentration of the developer, but with great dilutions the speed rapidly falls off. Sodium hydroxide acts as a stronger base than potassium hydroxide, but sodium carbonate is weaker than potassium carbonate; trisodium orthophosphate is a weak base, and the amines strong bases. In presence of equal proportions of alkali, an ortho-compound develops more rapidly than a para-compound, whilst the introduction of a carboxyl or sulphonic group diminishes the speed of development, and an amino-group increases it. Halogen atoms introduced into the molecule of a developer show behaviour varying with the alkali employed.

T. H. P.

Polarisation Capacity. FRIEDRICH KRÜGER (*Zeit. physikal. Chem.*, 1903, 45, 1—74).—Starting with the theory of electrical double layers, the author has developed a theory of polarisation capacity, partly resembling that of Warburg in its formal expression, but more comprehensive, and capable of interpreting the behaviour of all electrodes. The capacity is definitely related to the frequency of the alternating current, and the change in this relationship with change of concentration may be correctly deduced from the author's theory. This has been verified by experiments with mercury electrodes immersed in (1) NH_2SO_4 , saturated with mercurous sulphate; (2) $\text{NKCNS} + \text{N}/100\text{HgCNS}$; (3) $\text{NKI} + \text{N}/100\text{HgI}_2$; (4) $\text{N K}_2\text{S} + \text{N}/100\text{HgS}$. It should be noted that the theory leads to correct results on both sides of the maximum in the surface tension. In considering the influence of dissociation on the phenomena of polarisation, the author adopts the hypothesis that the velocity of ionic reactions is not infinitely great, but commensurable with the period of the alternating current.

J. C. P.

Absolute Potential of the Calomel Electrode. WILHELM PALMAER (*Zeit. Elektrochem.*, 1903, 9, 754—757).—The method used is based on Nernst's theory, according to which the drops of mercury of a dropping electrode will be positively charged in a solution in which the osmotic pressure of the mercury ions is greater than the solution pressure of mercury and *vice versa*. Hence, by gradually diminishing the concentration of the mercury ions in the solution, a point will be reached at which the direction of the current flowing between the dropping electrode and a stationary electrode (of mercury) changes, and at this point the *P.D.* between mercury and the solution is zero. The *E.M.F.* of a cell containing such a zero mercury electrode and a calomel electrode will obviously be the absolute potential of the calomel electrode (allowance having been made, of course, for the small *P.D.* at the junction of the two electrolytes).

Two solutions were found which gave no *P.D.* with mercury, the first contained potassium cyanide, the second hydrogen sulphide; in no other way was it possible to reduce the concentration of the mercury ions sufficiently. The *P.D.* of the *N*/10 calomel electrode was found to be -0.574 and -0.570 volt by means of the two solutions. T. E.

Behaviour of Unattackable ("unangreifbarer") Anodes, especially in the Electrolysis of Hydrochloric Acid. ROBERT LUTHER and F. J. BRISLEE (*Zeit. physikal. Chem.*, 1903, 45, 216—234).—When in an electrolytic cell containing hydrochloric acid a gradually increasing anode potential difference is applied, the current strength after its first rise remains constant for an interval, subsequently increasing again (compare Müller, Abstr., 1901, ii, 219; *Zeit. Electrochemie*, 1902, 8, 426). According to earlier workers, the existence of such a horizontal part in the *P.D.*-current curve means that the ion primarily concerned in the electrolysis is exhausted. In the experiments carried out by the authors, the Cl' ions cannot have been exhausted, and they suggest that there is probably something else in the solution, which is in equilibrium with the Cl' ions, and primarily liberated at the anode, and to the exhaustion of which is due the constant value ($i_{\text{lim.}}$) of the current strength. The experiments described show that $i_{\text{lim.}}$ is proportional to the second power of the Cl' concentration, and to account for this the authors assume the existence of an ion Cl_2'' .

The condition and previous history, however, of the platinum anode is an all-important factor. When the anode *P.D.*, after a gradual increase, is gradually diminished, without break of current, the corresponding variation of the current strength is not always that given by the first *P.D.*-current curve. The current strength may fall away rapidly almost to zero, the electrode having become "passive." If, while the electrode is still passive, the *P.D.* is again increased, the horizontal portion of the *P.D.*-current curve cannot now be obtained. This passive condition is due to a superficial change of the platinum anode, and has nothing to do with the solution. It disappears immediately if the current is broken, and if the anode *P.D.* is allowed to fall below 1.6 volt, a passive electrode becomes spontaneously active. Further, if the change of *P.D.* is reversed before $i_{\text{lim.}}$ is reached, the passive condition does not set in. The authors can thus distinguish three states of the platinum surface. The production of the passive condition does not depend on the presence of Cl' ions, but begins in acid solutions at about 1.9 volt and vanishes at about 1.6 volt.

The evolution of chlorine in hydrochloric acid solution at 1.66 volt is secondary, for it is possible, when anodes of carbon or iridium are used, to obtain *P.D.*-current curves of quite different form. Iridium does not exhibit the passivity spoken of above. J. C. P.

Theory of Electrolytic Dissociation in Solvents other than Water III. Influence of the Solvent on the Transport Numbers. GIACOMO CARRARA (*Gazzetta*, 1903, 33, i, 241—311. Compare Abstr., 1896, ii, 511, and 1897, ii, 471).—The author has determined the transport numbers in methyl alcohol solutions of different dilutions of: silver, copper, cadmium, and lithium nitrates; silver, copper, cadmium, and lithium chlorates; cupric and cadmium chlorides;

cadmium, lithium, tetraethylammonium, and trimethylsulphine iodides; copper and cadmium acetates and copper sulphate.

It is found that the transport numbers vary very greatly with the concentration and that they often show a similar behaviour, as is seen with cadmium iodide and similar salts, the values for which indicate the existence of complex ions in solution. The power of forming these complex ions, which may be given by salts containing only two different ions, varies very considerably for different salts.

On comparing the transport numbers for one and the same salt in aqueous and methyl alcoholic solutions, it is seen that the difference between them is, in the majority of cases, very small and, in general, of the same order of magnitude as the differences obtained by a change of concentration. As a rule, the transport numbers of anions are slightly higher in methyl alcohol than in water, and only in exceptional case is the reverse true. For methyl alcohol solutions, indeed, the transport numbers mostly behave just as they do in more concentrated aqueous solutions, but with lithium chlorate and cadmium chloride and iodide the reverse holds.

From these considerations, the conclusion may be drawn that the transport numbers of the ions of an electrolyte tend towards the same value, whatever be the solvent in which it is dissolved; in other words, if the dilution is sufficiently great and if no secondary reactions intervene, the transport numbers of an electrolyte are the same in all solvents.

T. H. P.

Direct Measurement of Transport Numbers. R. B. DENISO (*Zeit. physikal. Chem.*, 1903, 44, 575—599).—The author's method is practically that described by Steele (*Abstr.*, 1902, ii, 241. Compare also Abegg and Gaus, *ibid.*, 442), and it is shown that if allowance is made for the electrical endosmose, very accurate results can be obtained for the simple salts of the alkali metals, lithium excepted. Lithium chloride, as noted also by previous observers, exhibits an increase in the transport number for the anion with increasing concentration. In the case of salts that form complexes or undergo hydrolysis, the values obtained for the transport numbers do not agree with those given by Hittorf, although there is a parallelism between the two series. The transport numbers obtained for such salts cannot be regarded as absolutely correct until the influence of a complex ion on the ionic boundary has been mathematically treated.

The values obtained for transport numbers in gelatin solution are the same as those obtained in aqueous solution, provided the gelatin solution is liquid; the gelatin concentration, further, is immaterial. In solidified gelatin, the transport numbers are different, and it appears that under these conditions the velocity of the cations is retarded relatively to that of the anions, so that in solidified gelatin the transport number for the anion is too large. A similar phenomenon is observed in very concentrated aqueous solutions, and it is therefore probable that in these two sets of cases the specific frictional coefficient of the ions, as well as the formation of complexes, is a deciding factor. The author considers it probable that gelatin enters into combination with certain salts, forming complex cathions.

J. C. P.

The Gaseous-Liquid State. A. N. SCHÜKAREFF (*Zeit. physikal. Chem.*, 1903, 44, 548—562).—The author has determined the mean specific heat of isopropyl alcohol, acetone, methyl alcohol, and ether between the ordinary and the critical temperatures. Thence he has calculated the 'critical heat,' that is, the heat necessary to raise 1 gram-mol. of a substance from the ordinary to the critical temperature. It is found that the value of the critical heat so obtained is dependent on the final density of the substance at the critical temperature. This variation in the critical heat is brought into relation with the quantity a/v^2 in van der Waals' equation, but the experimental results do not tally with the theory.

Experiments were also made in which the mean specific heat of ether was determined between the ordinary temperature and the temperatures 96°, 190°, and 240°. Of these results, only those obtained at 240° gave a constant value for the a of van der Waals' equation. J. C. P.

Is the Coefficient of Magnetic Susceptibility for Iron and Manganese Salt Solutions Dependent on the Field Strength? ADOLF HEYDWEILLER (*Ann. Physik*, 1903, [iv], 12, 608—621).—For small values of the field strength, the coefficient is practically constant. If, however, a large range of field strengths is considered, from 0.1 to 40,000 C.G.S. units, there is a marked variation in the coefficient for ferrous chloride and sulphate, manganese chloride and sulphate; this is especially so in the case of the sulphates, where the increase amounts to 30—40 per cent. This result points to the formation of complexes in the last-mentioned solutions. J. C. P.

Trouton's Law and other Constants observed at the Boiling Point. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 319—338).—The author finds the heat of vaporisation of ψ -cumene to be 73.7 Cals., from which Trouton's constant is calculated to be 20.0. For ethyl benzoate, the values are 64.4 Cals. and 19.9 respectively.

For normal liquids, Trouton's formula has the value 20.7 ± 0.8 , whilst the constant $T.dp/dt = 8350 \pm 200$. The relation between several other regularities, observable at the boiling point, is also shown.

The pressure-temperature curves for ethyl benzoate and dimethylaniline have also been determined, the results being as follows:

Ethyl benzoate.		Dimethylaniline.	
Pressure.	Boiling point.	Pressure.	Boiling point.
626.5 mm.	204.2°	571 mm.	183.3°
650 "	206.1	600 "	184.9
700 "	209	650 "	188.15
760 "	212.45	700 "	191.1
800 "	214.6	750 "	193.8
860 "	217.4	763 "	194.5

Heat of Sublimation of Carbon Dioxide and Heat of Vaporisation of Air. ULRICH BEHN (*Ann. Physik*, 1903, [iv], 12, 669—670).—By way of correction of a previous paper bearing the above title (*Abstr.*, 1900, ii, 260), the author points out that the specific volume of gaseous air at 760 mm. and -183° , calculated under the assumption that Gay Lussac's law of expansion is still valid at that temperature, should be 236. Further, if in the equation $Jr = T.s.dP/dT$ (*loc. cit.*) the value of dP/dT is taken as 90 mm./ 1° (see Fischer and Alt, this vol., ii, 72), s is found to be 222 (compare Dewar, *Abstr.*, 1902, ii, 304).

J. C. P.

Heat of Combustion of Hydrogen. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1903, 16, 214—228).—A full description of the bomb calorimetric method employed is given. As a mean of 14 experiments, the value obtained for the heat of combustion of one gram of hydrogen at constant pressure and formation of liquid water at 0° , and in terms of the calorie at 20° , was 33,993 cal., the experimental error being ± 16 . Collating the author's results with those which he considers most trustworthy obtained by other investigators, the value 34,020 is obtained.

A. McK.

Thermodynamics of Water Gas. The Equilibrium $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$. OSKAR HAHN (*Zeit. physikal. Chem.*, 1903, 44, 513—547).—The equilibrium referred to was studied at temperatures from 686 — 1405° , and was approached in many cases from both sides. The containing vessels were constructed of porcelain or quartz, and the method employed was to pass a constant stream of the initial gaseous mixture through the heated vessel, the issuing mixture being subjected to analysis. The establishment of equilibrium was accelerated by the presence of platinum, acting as a catalytic agent, and it was shown that the composition of the issuing mixture was within wide limits independent of the rate of passage of the gas. Such a method has this advantage, that the influence of the inner surfaces of the containing vessel is eliminated.

The law of mass action was experimentally verified up to 1400° . Up to 1100° , the variation of the equilibrium constant is represented by the equation, $\log K = -2232/T - 0.08463 \log T - 0.0002203T + 2.5084$, where $K = [\text{CO}][\text{H}_2\text{O}]/[\text{CO}_2][\text{H}_2]$. At higher temperatures, probably owing to dissociation, the equilibrium constant increases more slowly than the formula requires.

J. C. P.

Ebullioscopic Behaviour of Phenols, Alcohols, Oximes, and Acids in Benzene Solutions. EFISIO MAMELI (*Gazzetta*, 1903, 33, i, 464—494).—Making use of the boiling point apparatus devised by Oddo (*Abstr.*, this vol., ii, 60), the author has examined the behaviour of the following compounds in boiling benzene. Phenol, *p*-cresol, carvacrol, β -naphthol, catechol, and resorcinol; normal and secondary octyl, cetyl, benzyl, and cumyl alcohols; salicyl-, piperonal-, and camphor-oximes; acetic, monochloroacetic, monobromoacetic, trichloroacetic, propionic, butyric, lauric, pimelic, benzoic, salicylic, and thymotic acids. From the results obtained, the following conclusions are drawn.

The phenols and alcohols exhibit fairly normal behaviour in benzene solution; in very dilute solutions, their molecular weights are in general less than the normal value which is obtained in solutions of from 2 to 6 per cent. concentration; the molecular weights then increase with the concentration of the solution, but do not reach values much higher than the normal. The acids show abnormal behaviour, as has already been observed in cryoscopic measurements; in very dilute solutions, they give molecular increments of the boiling point, which more or less correspond with the calculated values, but are in some cases much higher; but as the concentration increases, the molecular weight increases in all cases until it often exceeds the value calculated for a double molecule; this anomalous behaviour, due to the presence of the carboxyl group, becomes more marked in the dicarboxylic acids. The oximes exhibit behaviour intermediate between that of the alcohols and phenols and that of the acids; in very dilute solutions, their molecular weight at first rises fairly rapidly until, with concentrations of from 2 to 4 per cent., the normal values are attained; after this, a gradual increase occurs, but the values never become very high. In compounds with mixed functions, such as salicylic and thymotic acids and salicyloxime, the carboxyl and oximido-groups exert their influence to a greater extent than the hydroxyl.

The differences existing between the behaviours of these different classes of compounds is well brought out by the graphical representation given of the results.

T. H. P.

Behaviour and Melting Points of some Organic Substances at very Low Temperatures. GIACOMO CARRARA and ANGELO COPPADORO (*Gazzetta*, 1903, 33, i, 329—353).—The authors have examined the behaviour at low temperatures of a number of alcohols and other organic compounds which were cooled in liquid air contained in vacuum vessels, the temperature measurements being made by means of thermo-electric couples. In some cases, the substances examined solidified in a crystalline form, but others, especially the higher alcohols, became viscous on cooling and solidified to vitreous masses, so that their melting points could be only approximately determined, whilst some compounds behaved in both these ways. This peculiar behaviour, which is similar to that of colloidal substances, is supposed by the authors to be due to the molecular association of the liquid, and as this association increases with fall of temperature, and probably does so very rapidly in the neighbourhood of the freezing point, it seems as if the alcohols which solidify to vitreous masses must, like colloidal substances, possess very complex molecules at low temperatures. Further, there seems to be a certain parallelism between this molecular complexity and the readiness of formation of super-cooled liquids.

As will be seen from the results given below, the methyl compounds examined invariably melt at higher temperatures than the corresponding ethyl derivatives. Melting points do not, however, generally show the regularities observed in other physical properties, owing to

the complications caused by the changes undergone by the molecular structure, &c.

The following summarises the results obtained :

Substance.	Melting points.	
	Crystalline modification.	Vitreous modification.
Methyl alcohol.....	- 94·0°	—
Ethyl „	- 112·0	—
Normal propyl alcohol	—	- 127°
isoPropyl „	- 85·8	- 121
Normal butyl „	- 79·9	- 122
isoButyl „	—	- 108
Amyl alcohol (γ -methylbutyl alcohol) ...	—	- 117·2
Normal heptyl alcohol	- 36·5	—
Normal octyl „	- 17·9	—
Allyl „	—	- 129
Methyl mercaptan	- 130·5	—
Ethyl „	- 144·5	—
Methyl sulphide	- 83·2	—
Ethyl „	- 99·5	—
Methyl ethyl sulphide.....	- 104·8	—
Methyl iodide	- 63·4	—
Ethyl „	- 105·0	—
n-Propyl „	- 97·8	—
Toluene.....	- 93·7	—
Carbon disulphide	- 108·6	—
Chloroform	- 62·2	—

T. H. P.

Freezing Points of Dilute Solutions. THEODORE W. RICHARDS (*Zeit. physikal. Chem.*, 1903, 44, 563—570).—A main disadvantage of the exact freezing point methods worked out by Jones, Loomis, Raoult, Nernst, and Abegg is the slowness with which equilibrium is established between the ice and the solution. The author points out that this can be remedied by having a large quantity of ice present, thus increasing the surface of the solid phase. Any method based on this principle involves, of course, the analysis of the solution subsequent to the determination of the freezing point. The experiments made by the author with potassium chloride were carried out in a litre Jena flask, immersed in a freezing mixture of about the same temperature as the contents of the flask. The method, as here described and tested, is capable of great accuracy, and the few results already obtained are in agreement with the dissociation hypothesis.

J. C. P.

Thermal Properties of Solids and Liquids. II. SILVIO LUSSANA (*Nuovo Cimento*, 1903, [v], 5, 153—179).—From the results of a large number of dilatometrical measurements of phosphorus and α -naphthol, the author draws the following conclusions.

The compressibility in the solid state, as in the liquid state, diminishes with increase of pressure; if the volume is represented by the formula $V = a + bp + cp^2$, p being the pressure and a , b , and c constants, it is found that b is always negative and c positive, and further that b and c increase with rise of temperature and are much greater for liquids than for solids. The coefficient of dilatation diminishes with increase of pressure. In a state of superfusion, a substance behaves as it does in the liquid state, and it seems further as if superfusion is facilitated by increase of pressure. The variation of volume during the act of fusion diminishes with increase of pressure and the coefficient of the variation continuously decreases.

T. H. P.

Influence of the Pressure and Temperature on the Coefficient of Compressibility of Mercury. P. CARNAZZI (*Nuovo Cimento*, 1903, [v], 5, 180—189).—The results of a large number of measurements show that the compressibility of mercury obeys the same laws as those governing other liquids.

Thus the coefficient of compressibility of mercury increases as the temperature rises, and for any given temperature diminishes with increase of pressure. According to Amagat's researches, the amount of this diminution for the liquids studied by him increases as the temperature rises, so that the coefficient of compressibility between 2500 and 3000 atmospheres' pressure is usually less than half of that between 1 and 500 atmospheres. In the case of mercury, it is not possible to assert the validity of such laws, but as regards the mean coefficient of dilatation, as a rule, this diminishes with increased pressure.

T. H. P.

Certain Regularities in the Molecular Volumes of Inorganic Salts in Aqueous Solution. CARL FORCH (*Ann. Physik*, 1903, [iv], 12, 591—601).—If a litre of a salt solution weighs s grams, then $m_w = (s - m_s A_s) / A_w$, where A_s and A_w are the molecular weights, m_s and m_w the number of molecules per litre, of salt and solvent respectively. Further, if it be assumed that both salt and solvent exist independently in the solution, $m_s \phi_s + m_w \phi_w = 1000$, where ϕ_s and ϕ_w are the molecular volumes of salt and solvent. By taking solutions of neighbouring concentration, two equations such as that just referred to are obtained, involving two known values of m_s and two of m_w . The values of ϕ_s and ϕ_w calculated from these two equations may then be regarded as the mean molecular volumes for the range of concentration involved. By using the data already available and solving series of equations, the author has traced the variation of the molecular volumes with the concentration. In the case of sugar solutions, ϕ_s is nearly independent of the concentration, and has a value not very different from the molecular volume of the solid. For phosphoric acid, ϕ_s increases somewhat with the concentration, but more conspicuous instances of this variation are found for solutions of electrolytes such as sodium chloride, sulphuric acid, and magnesium sulphate. That dissociation, however, is not the only determining factor is seen from the fact that of the three electrolytes mentioned

magnesium sulphate exhibits the greatest variation; indeed, for this salt, negative values of ϕ_s are obtained for concentrations below $N/10$.

In a similar manner, but with rather less detail, the variation of the molecular volume in solution has been studied for a large number of salts and compared with the molecular volume of the solid. The difference between the two molecular volumes ($m_s=1$) for salts containing sodium, potassium, and silver united with a univalent atom or radicle amounts to 7.6 ± 0.95 . For a number of salts containing bivalent metals united with univalent atoms or radicles, the difference is 12.4 ± 0.96 . For the sulphates of a number of bivalent metals, the difference is 18.6 ± 0.93 .

J. C. P.

Composition of the Surface Layers of Aqueous Amyl Alcohol. CLARA C. BENSON (*J. Physical Chem.*, 1903, 7, 532—536).—It is found, by the comparison of the surface tensions of the foam of aqueous solutions of amyl alcohol with those of the solutions themselves, that the concentration of the alcohol is greater in the foam than in the main bulk of liquid. In the case of a solution containing 4 c.c. of amyl alcohol per litre, the foam was found to contain 4.12, 4.09, 4.13, and 4.23 c.c. per litre. The comparison of surface tension was obtained from the size of the drops falling from a pipette (compare Abstr., 1900, ii, 713; this vol., ii, 281).

L. M. J.

Relations between the Properties of Different Substances as Cryoscopic Solvents and their Crystallisation Constants. I. GIUSEPPE BRUNI and MAURICE PADOA (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 119—128).—The authors have determined by Tammanu's method (Abstr., 1897, ii, 444) the velocity of crystallisation and the number of crystallisation nuclei formed at different degrees of supercooling for the following substances: apiole, which gives numbers agreeing with those found by Tammann (Abstr., 1899, ii, 548); α -naphthylamine, benzylideneaniline, [anethole, isoapiole, dibenzyl, triphenylmethane, stearic acid, α -nitronaphthalene, bromocamphor, chlorocamphor, 1-chloro-2:4-dinitrobenzene, 1-chloro-3:4-dinitrobenzene, 1-bromo-3-nitrobenzene, and 1-chloro-3-nitrobenzene. The results show that the velocity of crystallisation does not remain constant, but that it is probably influenced by factors which are not easily determined.

T. H. P.

Solid Solutions and Isomorphism. MAURICE PADOA (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 391—397).—It is known that the groups CH: and N: replace one another in both open and closed chain compounds yielding isomorphous substances, and the present work has been carried out to see whether similar isomorphism exists between heterocyclopolyazo-compounds and the corresponding homocyclic compounds. The results, given later, show that in general this cannot be said to be the case, although affirmative indications are not wanting.

2:5-Dimethylpyrazine exhibits normal cryoscopic behaviour in benzene, but in *p*-xylene, it gives molecular weights of 129—136 instead of 108.

In freezing naphthalene solution, quinoxaline, phthalazine, and quinoxaline give the molecular weights 139—144, 149—157, and 137—143 respectively, the theoretical value being 130; in diphenyl, however, these three compounds have normal molecular weights.

In quinoxaline, for which the molecular depression of the freezing point has the mean value. 89, naphthalene has the normal molecular weight.

Phenazone and naphthaquinoxaline exhibit normal cryoscopic behaviour in phenanthrene solution, whilst 1-phenylpyrazole has a molecular weight slightly higher than the normal value both in diphenyl and in naphthalene.

T. H. P.

Influence of Salts on the Solubility in Water of Hydrogen Sulphide, Iodine, and Bromine. WILLIAM H. McLAUCHLAN (*Zeit. physikal. Chem.*, 1903, 44, 600—633).—The vapour pressure of hydrogen sulphide in a number of salt solutions was determined by a dynamical method, and the solubility of hydrogen sulphide in these and other solutions was found by analytical methods. The agreement between the two sets of results demonstrates the validity of Henry's law for hydrogen sulphide in these cases. The solubility of iodine and bromine in these salt solutions was also determined, the object being to discover how far the solubility was affected by probable chemical interaction between the two dissolved substances. The only solutions in which bromine was less soluble than in water were those of potassium and sodium nitrate and sulphate; the solubility of iodine was diminished not only in these, but also in ammonium sulphate. The increased solubility of iodine and bromine in solutions of potassium and sodium chlorides is doubtless due to the formation of complexes, that is, to interaction between the two dissolved substances. It is further to be noted that ammonium salts in general raise the solubility both of bromine and iodine, a result for which probably the hydrolysis of the ammonium salt is responsible.

The influence of certain salts on the solubility of iodine was determined at several temperatures, and it was found that the temperature coefficient of the effect may be very small, even in cases where there is certainly chemical interaction.

The solubility of hydrogen sulphide and iodine in some mixtures (1) of acetic acid and water, (2) of alcohol and water, was determined. The results obtained were compared with the consequences of a chemical theory of solution, but the theory, although satisfactory in some respects, was in others in marked disagreement with experiment.

J. C. P.

Solubility Curves of some Substances in Sulphur Dioxide near its Critical Point. MIECZYSLAW CENTNERSZWER and IV. TETELOW (*Zeit. Elektrochem.*, 1903, 9, 799—802).—Anthracene, anthraquinone, and quinol are the substances used. They are very sparingly soluble in liquid sulphur dioxide at the ordinary temperature, but the solubility increases rapidly as the temperature approaches the critical point. The solubility measured is the mean solubility in the liquid and vapour; the quantity of sulphur dioxide

used was such that the meniscus was approximately in the middle of the tube at the critical temperature. Evidently the quantity of liquid placed in the tube will affect the mean solubility. If 0.35 of the volume of the tube is filled with sulphur dioxide, together with a quantity of anthraquinone, and the temperature is gradually raised, the following phenomena occur successively: (1) the liquid expands, then diminishes in volume owing to evaporation, and finally disappears at t_1 . (2) The quantity of anthraquinone continues to diminish, liquid appears again at t_2 . (3) The solid anthraquinone passes entirely into solution at t_3 . (4) The liquid phase disappears at t_4 . If the temperatures t_3 and t_4 are plotted against the quantities of anthraquinone used per 100 grams of sulphur dioxide, two curves are obtained which may intersect. The point of intersection gives the solubility of anthraquinone in the saturated vapour at one temperature. Similarly, if a larger fraction of the tube is filled with liquid sulphur dioxide, the vapour phase may disappear instead of the liquid one, in which case the solubility of anthraquinone in the liquid is obtained. The following points were determined. The solubility is expressed in grams of anthraquinone in 100 grams of sulphur dioxide.

Temperature.	Solubility in the	
	Liquid.	Saturated vapour.
162°	13.2	—
176	—	2.2
188	—	3.4

T. E.

Complex Silver Ions. HANS EULER (*Ber.*, 1903, 36, 2878—2885).—The abnormal curves obtained by Wuth (*Abstr.*, 1902, i, 594) for the solubility of silver haloids in methylamine and ethylamine solutions are not confirmed by the author's experiments, which show an approximate proportionality between the solubility of silver chloride and the concentration of the amine. This was also found to be the case for solutions of silver oxide in methylamine and ethylamine.

The author's experiments on concentration cells (this vol., ii, 544) have been extended to a greater range of concentrations (1 to 0.02 normal), and have confirmed the previous results. The silver ethylamine complex corresponds closely with the ammonia complex in its dissociation, and not, as might be expected, with methylamine. Further measurements with the base, $\text{Ag}(\text{NH}_3)_2\cdot\text{OH}$, give the value 4.1×10^{-8} for K .

The solubility of silver oxide and silver chloride in amine bases varies very little with the temperature. The value of K for the silver-methylamine complex is doubled by a rise of temperature of about 10°, that for silver ethylamine by a rise of 8°.

Experiments with silver-hydrocyanic acid indicate a value of about 1.5×10^{-21} for K .

C. H. D.

Tension of Bromine Vapour in Solutions of Hydrobromic Acid. N. P. RICHTER-RJEWSKAJA (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 441—449).—The author has measured, by Doyer's method (*Abstr.*,

1891, 387), the partial pressure of bromine in various concentrations in hydrobromic acid solution at 30° ; the acid solutions employed contained from 3.2 to 10 mols. of water per 1 mol. of hydrogen bromide, and the percentage of bromine in the solutions varied from 9.85 to 96.7. The numbers obtained lead to the following results. Solutions containing more than a certain proportion of bromine are not homogeneous, but only emulsions, as is shown by the constancy of the pressure; by centrifugal action, two distinct liquid phases can be separated. The more dilute the hydrobromic acid, the greater becomes the portion of the partial pressure curve in which no change of pressure occurs, owing to the diminished solubility of the bromine. After the bromine becomes completely dissolved, the curve indicates that chemical action takes place between the bromine and the hydrobromic acid.

T. H. P.

Eutectic and Transition Points in Binary Mixtures which yield Mixed Crystals. PIERRE DUHEM (*J. Chim. phys.*, 1903, 1, 34—56, 97—120).—The system considered is one of two components capable of forming two solid mixtures, H and H_1 , in which the ratios of the two components are S and S_1 , and a liquid phase in which the ratio is s . The first case considered is that in which the three phases coexist and the necessary conditions are obtained thermodynamically. The univariant system necessitates a fixed temperature, θ . The conditions for the existence of the bivalent systems containing liquid and H or liquid and H_1 , both necessitate $T > \theta$, whilst those for equilibrium of the two solid phases necessitate $T < \theta$, the concentrations in each case being a function of the temperature. Three cases exist in which (1) $S < s < S_1$, (2) $s < S < S_1$, (3) $S < S_1 < s$. The first case is that in which eutectic mixtures occur, and the form of diagrams representing the equilibrium is deduced and given. In cases 2 and 3, transition points are obtained and the diagrams are given in the paper. In the second paper, the work is extended to the case where a definite compound of the two components may also exist. The conditions for the various univariant and bivalent systems are similarly discussed and the diagrams given.

L. M. J.

Dissolution of Metals. II. TYCHO ERICSON-AURÉN and WILHELM PALMAER (*Zeit. physikal. Chem.*, 1903, 45, 182—198. Compare Abstr., 1902, ii, 64).—The rate of solution of zinc in sulphuric acid can be represented by a formula similar to that previously applied (*loc. cit.*) in the case of hydrochloric acid. The necessary data for sulphuric acid have been obtained from the work of one of the authors (Ericson-Aurén, Abstr., 1901, ii, 451), and the same value has been assigned to the resistance capacity as in the case of hydrochloric acid.

Earlier papers dealing with the rate of dissolution of zinc are discussed at some length, and, in particular, it is shown that Spring and Aubel's formula (Abstr., 1887, 1074), according to which the rate of dissolution is, *ceteris paribus*, proportional to the total acid concentration, is in general incorrect. De la Rive's experiments on the influence of foreign metals on the rate of dissolution of zinc are

shown to be in harmony with the author's local current theory. This theory is tested also in its relation (1) to the solubility of copper, mercury, and silver in nitric acid, (2) to the phenomenon of the induction period, and in both cases it is found to give an adequate interpretation. J. C. P.

Influence of the Medium on the Speed of Reaction of Certain Ketones with Phenylhydrazine. PAVEL IW. PETRENKO-KRITSCHENKO and A. KONSCHIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 404—406).—Petrenko-Kritschenko's previous measurements (this vol., i, 440) of the velocities of reaction between ketones and phenylhydrazine were made with aqueous alcohol as medium, and as a result of the present work the authors find that the regularities there observed do not hold with other solvents, those used being benzene, nitrobenzene, light petroleum (boiling at 50—77°), and glacial acetic acid. Working under the former conditions, the velocities of reaction after half an hour are given in the following table:

	Benzene.	Nitrobenzene.	Light petroleum.	Acetic acid.
Acetone	28.9	34.9	55.3	65.2
Diethylketone	2.2	8.2	9.3	48.7
cycloPentanone	10.8	10.6	31.3	83.8
Hexamethyleneketone	67.2	41	64.5	64
Suberone	17.4	22.8	31.5	76.8

T. H. P.

Reaction of Ketones with Potassium Hydrogen Sulphite. PAVEL IW. PETRENKO-KRITSCHENKO and E. KESTNER (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 406—408).—The velocities of combination of a number of open- and closed-chain ketones with potassium hydrogen sulphite have been determined by means of titration with iodine. The values obtained show that, in general, the velocity of reaction is greater for cyclic than for aliphatic ketones. The order of the ketones, with regard to their rates of reaction with phenylhydrazine (see preceding abstract), is not maintained in this case, possibly owing to the reversibility of the reaction with potassium hydrogen sulphite. T. H. P.

Characteristic of Reactions of Ketones. A. KLDIASCHWILI (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 515—518).—The author confirms the results obtained by Petrenko-Kritschenko and Eltschaninoff (*Abstr.*, 1901, i, 506). Measurements of the reaction velocities of phenylhydrazine with salts of acetonediacetic acid and of laevulic acid, the results of which are given later, indicate that, in general, the closing of the ring by a bivalent metal conditions an increase in the velocity of reaction, but in this the specific nature of the metal intro-

duced seems also to play a part. The percentages of change in an hour in the various cases were as follows :

Manganese acetonediacetate...	18.50	Calcium lævulate...	25.00
Magnesium	18.75	Strontium	21.00
Barium	14.50	Potassium	21.5
Potassium	10.00	Sodium	20.25
Sodium	13.75		

T. H. P.

Velocity of Polyphase Reactions. ANTONIO QUARTAROLI (*Gazzetta*, 1903, 33, i, 497—507).—The author calls attention to the complexity of uni- and bi-molecular reactions, which take place in two phases, and shows, in the case of such a unimolecular reaction, how to calculate the amounts of change occurring in each of the two phases,

As an example of a two-phase bimolecular reaction, the hydrolysis of methyl oxalate by ammonia is taken. Since the first part of the reaction, the formation of $\text{NH}_4\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{OMe}$ takes place very rapidly, and the values of K are hence practically those corresponding with the second phase, yet there is a sensible decrease in the values of the constant, especially during the first hour, owing to the fact that part of the alkali is still being used up in bringing about the first part of the hydrolysis. If, however, the time is calculated not from the beginning, but from a later point in the reaction, practically constant values of K are obtained.

The fact that in any unimolecular or bimolecular reaction the laws of ordinary monophase reactions are not obeyed indicates that intermediate compounds are formed, and from the persistence of such divergence (if not from the importance of the divergence), even when the time is calculated from an advanced stage of the reaction, an approximate idea may be obtained of the velocities of the first and second phases.

T. H. P.

Kinetics of Oxidation with Permanganate. NIKOLAI SCHILOFF (*Ber.*, 1903, 36, 2735—2751).—The experiments of Harcourt and Esson on the action of potassium permanganate on oxalic acid (*Phil. Trans.*, 1866, 201) have been extended by the author. The rate of the reaction between permanganate and oxalic acid, when the latter is in excess, at first gradually increases to a maximum and then regularly falls. The reaction proceeds according to the equation $dx/dt = kx(A - x)$, where A is the initial concentration of the permanganate, x the amount of permanganate converted, t the time, and k a constant. The reaction was also investigated in the presence of manganous salt, when it proceeded according to $dx/dt = k(B + x)(A - x)$, where B represents the concentration of the manganese sulphate added. The reaction between manganese dioxide and oxalic acid proceeds much more quickly than that between permanganate and oxalic acid; part of the manganese dioxide is at first very quickly reduced, after which the reaction proceeds much more slowly. When the proportion of oxalic acid to permanganate is less than two

mols. of the former to one mol. of the latter, the rate of reaction is quite regular and gradual, until a point is reached when the rate suddenly greatly increases and when a strong change of colour and a separation of manganese dioxide occurs. The theoretical bearing of this action is fully discussed in the paper.

The action of permanganate on formic acid has also been studied. At the start of the action, the permanganate is quickly reduced, after which the action practically ceases and the solution becomes brown with the separation of manganese dioxide. Formic acid reacts much more quickly with permanganate itself than with manganese dioxide. The reaction between permanganate and formic acid is accelerated when fluoride is present.

A. McK.

Hydrolysis of Trisaccharides by Dilute Acids. ALFRED WOGGINZ (*Zeit. physikal. Chem.*, 1903, 44, 571—574).—In this paper, the above type of reaction is dealt with entirely from the theoretical standpoint. The corresponding experimental work is not yet complete.

J. C. P.

Phenomena of the Setting and Swelling of Gelatin. PAUL VON SCHROEDER (*Zeit. physikal. Chem.*, 1903, 45, 75—117).—In order to study the changes taking place in gelatin solutions, the author adopts the method of tracing the change of viscosity. When a gelatin solution is heated at 100°, and samples are taken out at intervals and placed in a thermostat at 25°, their viscosity being determined five minutes later, it is found that the values of the viscosity diminish, as the duration of the heating at 100° increases, ultimately becoming constant. This change is attributed to a process of hydrolysis, and the course of the change is represented by a logarithmic formula. If, further, the viscosity of one of the samples above referred to is determined not only five minutes after its introduction into the thermostat, but at subsequent intervals, it is found that there is a gradual rise in the values obtained, and that the rate of this rise is closely related to the ability of the gelatin solution to set. Thus, if dR is the difference in the values of the viscosity measured after 5 and 60 minutes, and dt is the corresponding interval of time, it is found that when dR/dt for any gelatin solution is less than 0.0075, that solution will not set within 24 hours; when dR/dt is greater than 0.0095, setting takes place within that time. Experiments have been made in which varying quantities of the sulphates, nitrates, and chlorides of sodium, potassium, and ammonium, the chlorides and sulphates of lithium and magnesium, were added to the gelatin solution before treatment. With the exception of potassium and ammonium nitrates in normal solution, all these salts increase the viscosity of the gelatin solutions, magnesium salts exerting the greatest influence. The order of the ions arranged according to the magnitude of their influence is the same as that given by Wagner (*Zeit. physikal. Chem.*, 1890, 5, 31) in his study of the influence of salts on the viscosity of water. Salts are found to have but little effect on the process of hydrolysis referred to above, but they have a marked effect on the values of dR/dt . The nature of this effect is determined chiefly by the anion of the salt used. Thus dR/dt is

increased by the presence of sulphates, and the extent of the increase grows with the concentration of the salt. Chlorides and nitrates diminish dR/dt , and when the values of dR/dt are plotted against the concentration of the salt, the curves for the chlorides all show a minimum about $N/8$ concentration, followed by a maximum about $N/4$ concentration; the curves for the nitrates exhibit a minimum about $N/2$ concentration. These results are in agreement with those of other workers (Pauli, Abstr., 1900, i, 265; Levites, Abstr., 1902, ii, 312. Compare also Steele, Abstr., 1902, ii, 241).

The effect of hydrochloric acid and sodium hydroxide on the behaviour of gelatin solutions was similarly studied. The process of hydrolysis is accelerated by both hydrogen and hydroxyl ions, and the final value of the viscosity thus attained after hydrolysis is lower than that reached in pure or salt-containing gelatin solutions. Further, the final value of the viscosity after hydrolysis in presence of the hydrogen ion is not the same as that reached after hydrolysis in presence of the hydroxyl ion. Gelatin solutions containing acid or base have a lower value of dR/dt than the corresponding pure gelatin solutions.

In the second part of the paper, attention is drawn to a phenomenon connected with the swelling of gelatin that seems inconsistent with the second law of thermodynamics. A gelatin plate that has taken up its maximum quantity of water might be expected to remain unchanged when introduced into a space saturated with water vapour. This, however, is not so, and the swelling of the plate diminishes, water being given off. So also when a dry gelatin plate is placed in saturated water vapour, it swells up and a point is reached when its weight no longer increases; if it is then placed in water, a very considerable increase of weight is observed. From these observations, it follows that the vapour pressure of the swollen gelatin is greater than the vapour pressure of water. If the vapour pressure of the gelatin is artificially reduced by allowing it to swell in a salt solution instead of water, the plate shows an increase in weight when placed in water vapour, provided the salt solution has been strong enough. A 0.00001*N* sulphate solution is sufficient to produce this changed effect, and it is suggested that these experiments point to a very sensitive method of measuring small differences of vapour pressure.

J. C. P.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1903, 36, 3158—3163).—See this vol., i, 869.

Stirring and Cooling Apparatus. GIUSEPPE PLANCHER (*Gazzetta*, 1903, 33, i, 512—515).—This apparatus, which is for the purpose of stirring heated mixtures containing volatile liquids and condensing the vapour of the latter, consists of a cylindrical metal condenser dropping into the neck of the flask in which the reaction is carried on and provided with a flange to rest on the top of the neck. Passing down the axis of the condenser is a narrow aperture just wide

enough to allow of the introduction of a perfectly cylindrical glass tube; the upper end of the latter, above the top of the condenser, is fitted with a pulley so that it can be rotated, and to the lower end can be fitted any form of stirrer, that devised by Witt and having a spherical shape being especially suitable. T. H. P.

Inorganic Chemistry.

Formation of Ozone. EUGEN GOLDSTEIN (*Ber.*, 1903, 36, 3042—3046).—When a tube of fused quartz was exhausted until the pressure registered only a few mm. and then charged from an induction coil, an intense odour of ozone was observed in the surrounding atmosphere, and iodised starch paper was turned blue quickly. The odour of ozone was not perceptible when the pressure inside the tube exceeded a certain value; it was perceptible at very small pressures, and was most intense when the light from the discharge was at its brightest. The phenomenon is ascribed to the ultra-violet light rays of small wave-length penetrating the quartz and then converting the atmospheric oxygen into ozone.

A Geissler tube was exhausted, and oxygen was passed into it until the pressure registered several cm. The tube was then partially immersed in liquid air and charged from an induction coil. After $\frac{1}{2}$ min., the tube became luminous, and the pressure sank to about 0.1 mm. Oxygen was again introduced until the pressure was several cm. and the sparking continued. By repeated treatment in this manner, oxygen can be entirely converted into ozone, which was obtained as a dark blue liquid.

The spectrum of pure oxygen may readily be investigated by the aid of this method, since organic substances present are attacked by the ozone, even at the temperature of liquid air.

The liquid ozone obtained was not found to be spontaneously explosive. A. McK.

Formation of Dithionic Acid. UBALDO ANTHONY (*Gazzetta*, 1903, 33, i, 450—454).—The author criticises Meyer's work (this vol., ii, 18). T. H. P.

Preparation of Sulphamide. OTTO RUFF (*Ber.*, 1903, 36, 2900—2901. Compare Traube, *Abstr.*, 1893, ii, 268; Hantzsch and Holl, *ibid.*, 1902, ii, 14; and Divers and Ogawa, *Trans.*, 1902, 81, 504).—A solution of sulphuryl chloride in its own weight of chloroform is slowly dropped into a solution of ammonia in well-cooled chloroform, which is kept agitated. When the reaction slackens, the solution is again saturated with ammonia and the addition of the sulphuryl chloride solution continued. The two operations are alternated until

100 grams of the chloride have been added to each 400 grams of the original ammonia solution. The solid is removed and dried at 100° , thoroughly mixed with dry sand, and then extracted in a Soxhlet's apparatus for 4—6 hours with dry ethyl acetate. It melts at 93° (corr.).

J. J. S.

Attempts to prepare Nitrogen Fluoride. OTTO RUFF and E. GEISEL (*Ber.*, 1903, 36, 2677,—2681).—When a saturated aqueous solution of ammonium fluoride is electrolysed in a glass U-tube between platinum electrodes, contrary to Warren's statement (*Abstr.*, 1887, 770), the formation of nitrogen fluoride cannot be observed; the liquid round the anode contains subsequently considerable quantities of hydrofluoric and hydrofluosilicic acids, and that round the cathode the ammonium salts of these acids. The nitrogen evolved at the anode does not contain a trace of fluorine. When the electrolysis is carried out in a leaden U-tube between lead electrodes, pure hydrogen is evolved at the cathode, and a mixture of hydrogen and oxygen containing no nitrogen at the anode, whilst a paste of lead fluoride is formed inside the tube; here, again, nitrogen fluoride is not formed. Warren's nitrogen fluoride probably consisted of nitrogen chloride produced from ammonium chloride contained in the salt he electrolysed.

When ammonium hydrogen fluoride, dissolved in anhydrous hydrofluoric acid, is electrolysed, pure fluorine only is formed.

W. A. D.

Preparation of Nitrosyl Chloride. LUIGI FRANCESCONI and G. BRESCIANI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 75—80).—The most suitable method of preparing pure nitrosyl chloride is by the action of nitric oxide on chlorine in presence of animal charcoal, and a theoretical yield may be obtained if the following conditions are fulfilled. The charcoal should be finely granular, and should be dried at 150° . The gases and also the interior of the apparatus used should be dry, and the gases should be passed over the charcoal in a regular stream containing two vols. of nitric oxide to one of chlorine. The temperature of the charcoal must lie between 35° and 70° , and is best kept at 40 — 50° . The chlorine is most suitably obtained by the action of fuming hydrochloric acid on manganese dioxide. A slight pressure favours the formation and condensation of the nitrosyl chloride.

As thus prepared, nitrosyl chloride condenses on cooling to a ruby-red, mobile liquid boiling at -5.6° under 751 mm. pressure. When cooled by means of liquid air, it forms a lemon-yellow, crystalline mass melting between -61° and -60° . Its critical temperature is 163 — 164° .

T. H. P.

Preparation of Potassium Oxide. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 143216).—Potassium oxide is readily oxidised, either by air or potassium nitrate, to the peroxide. However, potassium nitrate may be converted into oxide by fusion with metallic potassium in the proportions required by the equation $\text{KNO}_3 + 5\text{K} = 3\text{K}_2\text{O} + \text{N}$,

air being excluded as completely as possible. The method is similar to that employed in the preparation of sodium oxide (this vol., ii, 646). Potassium nitrite may be employed in place of the nitrate. Mixtures of potassium and sodium oxides may be prepared in a similar manner.

C. H. D.

Solubility Curve of Sodium Tetraborate. DAVID W. HORN and ELIZABETH M. VAN WAGENER (*Amer. Chem. J.*, 1903, 30, 344—350).—From measurements of the tension of aqueous vapour over borax, Lescœur (*Abstr.*, 1898, ii, 108) has found that the transition of the decahydrate into the pentahydrate is complete at 60°. An irregularity in the solubility curve is, therefore, to be expected at this temperature. When, however, the solubility of borax as determined by Poggiale (*Ann. chim. phys.*, 1843, [iii], 8, 467) is represented in graphic form, the resulting curve undergoes no sudden change in direction throughout its course. The authors have, therefore, redetermined the solubility of borax at various temperatures between 0° and 100° and have plotted the results as a curve. It is found that at about 60—62° a definite change occurs in the direction of this curve. The existence of the penta- and deca-hydrates is thus confirmed, but no evidence is obtained of the existence of a hexahydrate.

E. G.

Determination of the Molecular Weight of Metallic Chlorides. LEOPOLD RÜGHEIMER (*Ber.*, 1903, 36, 3030).—The molecular weights of metallic chlorides can be determined from the boiling point of their solutions in bismuth chloride, which boils at 447° and has a normal vapour density at 490°. The method adopted was to determine the influence of pressure on the boiling point of the solvent and to calculate the vapour pressure of the solution from the elevation of the boiling point; the molecular weight was then calculated directly from the vapour pressure, and the use of a boiling point constant was thus avoided. The results obtained were:

	M. W. (found).	M. W. (calc.).
NaCl.....	64·2	58·5
BaCl ₂	209·4	208·3
SrCl ₂	163·9	158·5
MnCl ₂	129·8	125·9
CoCl ₂	127·6	129·9
CuCl ₂	127·2	134·5

T. M. L.

Silver Hyponitrite. EDWARD DIVERS (*Ber.*, 1903, 36, 2878).—A reply to Wieland (this vol., i, 691). The author distinctly stated (*Proc.*, 1898, 14, 224) that silver hyponitrite, when heated, is decomposed without explosion.

T. M. L.

Electrolytic Production of Calcium. JOSEPH H. GOODWIN (*J. Amer. Chem. Soc.*, 1903, 25, 873—876).—An electric furnace is described for the production of calcium from fused calcium chloride.

For details, the description and diagram in the original must be consulted. E. G.

Solubility of Calcium Hydroxide in Solutions of Alkali Hydroxides and the Rendering Caustic of Alkali Carbonates. ALEXANDRE D'ANSELME (*Bull. Soc. chim.*, 1903, [iii], 30, 936—939).—Determinations of the solubility of calcium hydroxide in solutions of sodium hydroxide of various concentrations at temperatures between 20° and 100° show that the solubility decreases both with rise of temperature and with increase in concentration of the alkali hydroxide. The rendering caustic of alkali carbonates by calcium hydroxide becomes, therefore, less effective at higher temperatures and as the concentration of the alkali hydroxide increases. T. A. H.

Action of Metallic Magnesium on Aqueous Solutions. CHARLOTTE F. ROBERTS and LOUISE BROWN (*J. Amer. Chem. Soc.*, 1903, 25, 801—809. Compare Kablenberg, *Abstr.*, this vol., ii, 426).—Magnesium has no action on distilled water which has been freed from gases by boiling and afterwards cooled out of contact with air. It reacts, however, with undistilled water, with unboiled distilled water, or with water which has been boiled and afterwards charged with oxygen or carbon dioxide, varying amounts of hydrogen being liberated.

Magnesium reacts with aqueous solutions of the chlorides of sodium, potassium, magnesium, barium, calcium, and strontium, and slowly with the sulphates of magnesium, sodium, and potassium with the evolution of an equivalent quantity of hydrogen. The action of the chlorides is much more rapid than that of the corresponding sulphates. The rate of action in the case of a metallic chloride is dependent on the concentration. The maximum rate is greater and more quickly attained in a strong solution than in a weaker one, but the length of time required for the completion of the reaction does not differ much in the two cases. With solutions of metallic chlorides of equivalent strength, the rapidity of action is in the following order: magnesium, barium, strontium, calcium, sodium, potassium.

The relation between the time and the amount of gas collected in these experiments is represented by a series of curves which show that the chlorides of sodium and potassium are similar in their action, as also are the chlorides of calcium and strontium, whilst the action of the barium salt is more like that of magnesium chloride than that of the other alkaline earth chlorides. E. G.

Magnesium Suboxide. G. BABOROVSKÝ (*Ber.*, 1903, 36, 2719—2720).—From electrolytic experiments, the author deduces a small value for the valency of magnesium; he obtained a deposit which is easily oxidised in moist air, yields pure hydrogen with water and with acids, contains no silicon, and can only be either a mixture of magnesium oxide and magnesium or a magnesium suboxide. The latter possibility is considered the more likely; the suboxide probably has the composition Mg_8O_5 (or, possibly, Mg_3O_2). The substance obtained by Christomanos (this vol., ii, 546) has the same composition. A. McK.

Action of Tartaric Acid and its Salts on Lead Sulphate. C. REICHARD (*Chem. Zeit.*, 1903, 27, 924—925, 943—944).—Lead sulphate is insoluble in potassium and sodium tartrates, but is soluble in their double tartrates with ammonium. Ammonia itself does not dissolve the compound, but if added to a solution of sodium tartrate containing lead sulphate in suspension solution takes place. The solution of lead sulphate in neutral ammonium tartrate seems to contain part of the lead as a basic salt, for on adding a small quantity of potassium dichromate the precipitate formed at first consists of the orange-red basic lead chromate.

L. DE K.

Plumbic Salts. KARL ELBS and R. NÜBLING (*Zeit. Elektrochem.*, 1903, 9, 776—782. Compare Abstr., 1901, ii, 99).—Concentrated hydrochloric acid is electrolysed at 10°, with an anode compounded of two lead plates and a carbon plate, and a lead cathode surrounded by a porous pot. Matters are arranged so that one-half of the current passes through the lead part of the anode and the other half through the carbon plate, where the current densities are 0.007 and 0.04 ampere per sq. cm. respectively. In these circumstances, the lead chloride formed at the lead anode is converted into plumbic chloride by the chlorine produced at the carbon anode. The yield of the acid H_2PbCl_6 is 70—80 per cent. of the theoretical quantity. From the orange-yellow solution, the ammonium, pyridine, and quinoline salts may be precipitated by adding the corresponding chlorides. These salts are fairly stable and may be heated for several hours at 115°, 68°, and 70° respectively without decomposition. The solutions, in a small quantity of water, decompose slowly, forming chlorine and hypochlorous acid and lead chloride, whilst a large quantity of water or a dilute solution of an alkali gives lead peroxide. In crystalline form, the three double salts resemble the corresponding platinum compounds; 100 c.c. of 20 per cent. hydrochloric acid dissolve 0.25 gram of the ammonium salt, 0.2 gram of the pyridine salt, and 0.1 gram of the quinoline salt. Potassium plumbichloride, K_2PbCl_6 , forms lemon-yellow octahedra which can only be preserved under concentrated hydrochloric acid. Electrolysis of hydrobromic or hydriodic acids under the conditions above described did not yield the corresponding bromide or iodide. The quinoline salts described by Classen and Zahorski (Abstr., 1893, ii, 464) appear to be isomeric substances, possibly of the constitutions $2\text{C}_9\text{H}_7\text{N}, \text{HBr}, \text{PbBr}_2, \text{Br}_2$ and $2\text{C}_9\text{H}_7\text{N}, \text{HBr}, \text{PbI}_2, \text{I}_2$. With very dilute solutions of chromic acid and lead electrodes, lead chromate alone is obtained, with stronger solutions (up to 40 or 50 per cent.), a mixture of lead chromate and lead peroxide is formed at the anode. With very concentrated solutions, however (130 grams of CrO_3 per 100 c.c.), a solution is obtained which evolves oxygen when kept and deposits lead pyrochromate, PbCr_2O_7 . The quantity of oxygen evolved is in agreement with the equation $\text{Pb}(\text{Cr}_2\text{O}_7)_2 = \text{PbCr}_2\text{O}_7 + 2\text{CrO}_3 + \text{O}$. When orthophosphoric acid of sp. gr. 1.75 is used as the anode liquid, it becomes dark brown and contains a considerable quantity of lead. After some days, this brown liquid deposits most of the lead in the form of a mud, which, after draining on porous earthenware, consists of fairly pure plumbic phosphate, $\text{Pb}(\text{H}_2\text{PO}_4)_4$. This salt is fairly stable.

When hydrosilicofluoric acid is used as the electrolyte, the lead dissolves readily at the anode, but there is no indication whatever of the formation of a plumbic salt. T. E.

Crystallised Polysulphides of the Heavy Metals. KARL A. HOFMANN and F. HÖCHTLEN (*Ber.*, 1903, 36, 3090—3092).—The copper ammonium polysulphide described by Peltzer (*Annalen*, 1863, 128, 180), Bloxam (this Journal, 1865, 18, 94), and Gescher (*Annalen*, 1867, 141, 350), to which the formula $2\text{CuS}_3 \cdot (\text{NH}_4)_2\text{S}$ has been given, is now shown to have the composition CuS_4NH_4 . When decomposed by hydrochloric acid in an atmosphere of carbon dioxide, it gives a green solution which turns blue on exposure to the air. It is probably the copper ammonium salt of Küster's hydrogen tetrasulphide.

Platiniammonium polysulphide, $\text{PtS}_{15}(\text{NH}_4)_2 \cdot 2\text{H}_2\text{O}$, obtained from ammonium polysulphide and chloroplatinic acid, forms large, red, glistening, rhombic crystals, and when dry is quite stable.

A gold compound, AuS_3NH_4 , has also been obtained in the form of flat, yellow, rhombic prisms. All these compounds are transparent, and not opaque like the simple sulphides of the same metals. *Thullium pentasulphide*, Tl_2S_5 , forms glistening, black, opaque prisms. J. J. S.

Double Cæsium and Mercuric Chlorides and their Solubility. HARRY W. FOOTE (*Amer. Chem. J.*, 1903, 30, 339—344).—The method already described for investigating the double salts formed in mixtures of two single salts (this vol., i, 797) has been applied to the double cæsium and mercuric chlorides. The results show that the five double salts described by Wells (*Abstr.*, 1892, ii, 68) and no others are formed at 25°. It was shown by Wells that the double salt, $\text{CsCl} \cdot \text{HgCl}_2$, occurs in two crystalline modifications, one form crystallising in cubic, and the other in rhombic, crystals. It is found that both forms can exist in equilibrium only under one definite set of solubility conditions; the relative proportion of the two salts in solution determines which form is stable. E. G.

Formation of Mixed Crystals of Mercuric Chloride and Iodide. MAURICE PADOA and C. TIBALDI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 158—166).—The melting point curve of mixtures of mercuric chloride and iodide consists of two branches meeting in a eutectic point at about 145°, which is 109° below the melting point of the iodide and 132° below that of the chloride. The nature of the curve indicates that a discontinuous series of mixed crystals is formed but no chloro-iodide. From a liquid mixture of the iodide and chloride having the composition represented by the eutectic point, two kinds of mixed crystals separate, one containing about 50 per cent. (in mols.) and the other about 70 per cent. of the chloride.

The change in colour from yellow to red of the crystalline mass obtained by solidifying liquid mixtures of the two salts, which takes place very quickly at the ordinary temperature, even when only 1.3 mols. per cent. of the iodide are present, indicates that some transformation goes on in the solid state. This is found to be due to the conversion of

the mixed crystals, which are stable at a high temperature, into red crystals rich in iodide and pure crystals of the chloride.

On subliming mixtures containing, in one case, 66·36, and, in another, 32·87 and 41·61 per cent. of the iodide, it is found that the sublimed crystals contain 45·61, respectively of iodide, the coefficient of distribution, α , having the values 0·68 and 1·21 in the separate cases. This is explained by regarding mercuric chloride and iodide as giving two distinct series of mixed crystals, so that the behaviour on sublimation cannot be so simple as when only one such series is formed. T. H. P.

Mercurous Sulphide. CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1903, 25, 799—800. Compare Baskerville and Miller, *Abstr.*, 1898, ii, 586).—Metallic mercury was left in contact with pure sulphuric acid (99·65 per cent.) in a glass-stoppered bottle for five years. On opening the bottle, sulphur dioxide escaped, and the surface of the mercury was found to be coated with brownish-black flakes or plates consisting of mercurous sulphide. When mercurous sulphide is heated in a closed tube, it first becomes white owing to oxidation, then slightly yellow, and afterwards melts to a dark orange-brown liquid which, on cooling, changes to a white solid. E. G.

Autoxidation of Cerous Salts. EMIL BAUR (*Ber.*, 1903, 36, 3038—3041).—From experiments on the amount of oxygen absorbed by alkaline cerous solutions, Engler (this vol., ii, 599) concludes that the oxidation takes place in the proportion 1Ce : 10. This is not in agreement with the author's conclusion (*Abstr.*, 1902, ii, 398) that the proportion is 1Ce : 20. The latter view is confirmed by experiments on the oxidation of cerous chloride in potassium carbonate solution.

A. McK.

Absorption Spectra of Didymium Salt Solutions containing Phosphoric Acid. Didymium Orthophosphate. ANTON WAEGNER (*Ber.*, 1903, 36, 3055—3058).—When an excess of phosphoric acid is added to a solution of didymium chloride, the absorption spectrum of the resulting clear solution is very different from that of a neutral solution of didymium chloride.

Didymium orthophosphate, $\text{DiPO}_4 \cdot \text{H}_2\text{O}$, prepared by adding water to a solution of a didymium salt containing phosphoric acid, or by warming such a solution, is a white powder, insoluble in water and in dilute acids. Its characteristic absorption spectrum is described. Strong sulphuric acid converts didymium orthophosphate into a mixture of didymium sulphate and metaphosphate. A. McK.

Solubility of the Hydroxides of Aluminium, Beryllium, and Indium in Ammonia and Amines. CARL RENZ (*Ber.*, 1903, 36, 2751—2755).—When a solution of aluminium nitrate is precipitated by an excess of ammonia, a small quantity of aluminium hydroxide remains dissolved, but freshly precipitated and washed alumina is quite insoluble in ammonia. When a solution of potassium aluminate is precipitated by the calculated quantity of ammonium chloride and a large excess of ammonium hydroxide is rapidly added, the precipitate

completely redissolves. The modification of aluminium hydroxide soluble in ammonia is best prepared by addition of the calculated quantity of ammonium sulphate to a solution of barium aluminate to which an excess of ammonia has been added. On filtering off the barium sulphate, a clear solution is obtained, containing 0.1 gram of alumina in 50 c.c., and on evaporation leaving the hydroxide as a white, not horny mass, dissolving less readily in acids than the ordinary modification. Aluminium hydroxide dissolves readily in ethylamine, methylamine, diethylamine, and dimethylamine solutions, even in presence of some hydrochloride of the base.

Beryllium hydroxide is insoluble in ammonia and in solutions of the bases named. Ethylamine may be employed to effect a very rapid and exact quantitative separation of aluminium from beryllium, a concentrated solution of the salts being shaken with an excess of ethylamine and filtered. The whole of the aluminium is present in the filtrate.

The behaviour of indium hydroxide towards amines approaches that of iron rather than that of aluminium; ethylamine or methylamine dissolves a small quantity, but this is completely precipitated by the hydrochloride of the base (compare also this vol., ii, 548).

C. H. D.

Properties and Constitution of Manganese Steels. LÉON GUILLET (*Compt. rend.*, 1903, 136, 480—482. Compare Osmond, *Abstr.*, 1894, ii, 283; 1899, ii, 351; 1901, ii, 400).—The structure of manganese steels is very similar to that of nickel steels (this vol., ii, 297), but the effect produced by the addition of manganese is relatively greater than that produced by the addition of nickel. "Low carbon" steels, containing from 0 to 5 per cent. of manganese, and "high carbon" steels, containing 0 to 3 per cent. of manganese, have a perlitic structure (Group I). The same two classes containing respectively 5 to 12 per cent. and 3 to 7 per cent. of manganese consist of martensite or troostite (Group II), whilst with higher proportions of manganese than these γ -iron is produced (Group III). As in the case of nickel steels, Group II may be further sub-divided according as the structure is "iron and martensite," "martensite," or "martensite and γ -iron."

The changes produced in manganese steels by tempering, annealing, &c., are identical with those observed in the case of nickel steels (this vol., ii, 297).

The breaking stress of perlitic steels is higher than that of ordinary carbon steels and increases with the percentage of manganese present. They also offer a high resistance to shock, indicating, as has already been established by Hadfield, that the addition of manganese does not weaken steel so long as a martensite structure is not produced. The principal mechanical properties of manganese steels are tabulated in the original.

T. A. H.

Electrolytic Reduction of Acid Solutions of Molybdic Anhydride. Compounds of Molybdenum Trichloride. I and II. ALBERTO CHILESOTTI (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 22—26 and 67—73).—The electrolysis of either a hydrochloric acid

solution of molybdic anhydride or a solution of ammonium molybdate in dilute sulphuric acid, using a mercury cathode, gives rise to a solution of molybdenum trichloride, which, when prepared in the dry way, cannot be dissolved unchanged. The close analogy existing between chromium and molybdenum is confirmed by the properties of this trichloride and by the composition of the double chlorides.

The potassium and ammonium double salts are extremely soluble in water, giving intensely red solutions, whilst those of rubidium and caesium are less soluble; these compounds are practically insoluble in alcohol. The aqueous solutions rapidly decompose, but solutions in dilute hydrochloric, sulphuric, or acetic acid are more stable. With concentrated sulphuric acid, these salts give emerald-green solutions. The reactions of solutions of the double compounds with salts of mercury, lead, copper, and silver seem to indicate that all these solutions contain a common complex anion. Oxidising agents decolorise these solutions, but the addition of quantities of nitric acid or hydrogen peroxide insufficient for complete oxidation gives, in the inverse order, the same colorations as are obtained in the reduction of solutions of molybdic anhydride.

The double salts of molybdenum trichloride with potassium chloride, K_3MoCl_6 , and with rubidium chloride, $Rb_2MoCl_5 \cdot H_2O$, form red crystals; with caesium chloride, three different crystalline forms of the compound, $Cs_2MoCl_5 \cdot H_2O$, are obtained; the ammonium chloride compound, $(NH_4)_2MoCl_5 \cdot H_2O$, separates as a brick-red powder.

T. H. P.

Phosphomolybdic Acid. MARIO G. LEVI and E. SPELTA (*Gazzetta*, 1903, 33, i, 207—226).—Analyses of several different specimens of carefully prepared and purified phosphomolybdic acid confirm the formula given to this acid by Finkener and by Gibbs, namely, $H_3PO_4 \cdot 12MoO_3 \cdot 29H_2O$.

The authors have also made cryoscopic, ebullioscopic, and conductivity measurements of solutions of this acid, and have studied its behaviour towards bases and indicators, its conductivity during neutralisation, and its influence on the catalysis of methyl acetate. From the results obtained, it is concluded that the union between the phosphoric and molybdic acids is a very unstable one, and is destroyed by the action of alkalis and also to some extent by water alone. By titrating with sodium hydroxide solution in presence of litmus, phenolphthalein, or rosolic acid, it is found that a molecule of the acid contains 27 replaceable hydrogen atoms, which is the number required on the supposition that the acid is resolved into phosphoric and molybdic acids. The occurrence of such resolution in alkaline solution is confirmed by the fact that phosphoric acid may be quantitatively precipitated in ammoniacal solution even in presence of molybdenum; further, with ammonia, solutions of phosphomolybdic acid give first a precipitate of phosphomolybdate which dissolves in the slightest excess of the ammonia, whilst phosphoric acid can only be precipitated by ammonium molybdate in strongly acid solutions, and the precipitate formed is soluble in ammonia. Hence, ammonia

resolves the ammonium phosphomolybdate into ammonium phosphate and molybdate.

The authors have not as yet explained the fact that 5 of the 27 replaceable hydrogen atoms are different from the remaining 22.

T. H. P.

Basic Salts of Quadrivalent Uranium. N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 513—515. Compare Abstr., 1902, ii, 506).—By the action of light on a solution of uranyl chloride in a mixture of alcohol and ether, in some cases, but not always, green crystals of the composition $\text{UCl}_4 \cdot 2\text{UO}_2 \cdot 13\text{H}_2\text{O}$ are formed. When dried over concentrated sulphuric acid, the salt loses $12\text{H}_2\text{O}$, and when heated at 100° it becomes brownish-black and assumes the composition $\text{UCl}_4 \cdot 4\text{UO}_2$. With ammonium oxalate, it yields an *oxalate* of the composition $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 2\text{UO}_2$, soluble in excess of ammonium oxalate.

T. H. P.

Radioactive Thorium. KARL A. HOFMANN and F. ZERBAN (*Ber.*, 1903, 36, 3093—3096. Compare Abstr., 1902, ii, 211).—The previous statement, that the radioactivity of freshly-precipitated thorium dioxide preparations depends on the percentage of uranium contained in the mineral from which the dioxide is obtained, is confirmed. All preparations when kept for 1.5 to 2 years become less active and then exhibit but very feeble β -activity, and at the same time the α -radiation is reduced to the value of that of uranium preparations and then remains practically constant. This residual activity cannot be destroyed by heating for 100 hours in the blow-pipe or by the high temperature produced by reduction with magnesium in an atmosphere of hydrogen. When thorium chloride is mixed with 50 times its weight of barium chloride and then precipitated with sulphuric acid, it does not entirely lose its activity. It is thought probable that the initial high activity is induced by the uranium in the original mineral. Thorium preparations obtained from minerals free from uranium are inactive.

A specimen of gadolinite from Sotersdale, when suddenly heated, glowed brightly and steam was evolved. The glowing was due to some exothermic chemical reaction and was not accompanied by any radioactivity. Specimens of actinium (Debiere, Abstr., 1900, ii, 20, 350), which in many respects resemble thorium preparations, may be kept for years and still be strongly active.

The oxalate of actinium is soluble in warm ammonium oxalate solution, but, unlike thorium oxalate, cannot be reprecipitated by the addition of ammonia or acids. The dried sulphate is only sparingly soluble in ice-cold water, and the ignited oxide dissolves readily in concentrated sulphuric acid. It differs from Giesel's emanation-substance (this vol., ii, 193) in its solubility in ammonium oxalate and the fact that it is precipitated with thiosulphate.

The equivalent for "actinium" has been found to be 63.32,

whereas that for pure thorium is 58.1 ($O=16$). The non-identity of thorium and actinium is not regarded as being fully established.

J. J. S.

Behaviour of the Vanadates in Aqueous Solution. P. DÜLLBERG (*Zeit. physikal. Chem.*, 1903, 45, 129—181).—It is well known that the process of neutralisation with acid or alkali can be traced by the change in the conductivity of the solution under investigation (compare, for example, Miolati and Mascetti, *Abstr.*, 1901, ii, 381). This method has been applied by the author in order to study the conditions of formation and transition of the various forms of vanadic acid. For the sake of comparison, the neutralisation-conductivity curves for chromate and phosphate have also been determined, and the neutralisation involved has also been followed with the aid of ordinary indicators.

Sodium metavanadate, according to the freezing point determinations carried out by the author, has the formula $Na_3V_3O_9$. Sodium orthovanadate in solution is completely resolved into pyrovanadate and sodium hydroxide according to the equation: $2Na_3VO_4 + H_2O = Na_4V_2O_7 + 2NaOH$. The ions existing in a pyrovanadate solution are $V_2O_7^{''''}$, and not the acid ions $HVO_4^{''}$, as might have been possible.

The salts of the so-called condensed vanadic acids are to be regarded as the acid salts of hexavanadic acid, $H_4V_6O_{17}$, which has been prepared by the action of hydrogen peroxide on vanadium pentoxide. Roscoe's tetravanadate has the formula $Na_3HV_6O_{17}$, and should therefore be called tertiary hexavanadate; similarly, the hexavanadate, $Na_2V_6O_{16}$, is found to be identical with $Na_2H_2V_6O_{17}$, that is, secondary hexavanadate. The neutral hexavanadate, $Na_4V_6O_{17}$, is not stable in solution, and breaks up into $Na_3HV_6O_{17} + NaOH$. From these hexavanadates, free hexavanadic acid is precipitated by the addition of mineral acids. It decomposes, especially if the solution is heated or excess of mineral acid added, yielding the pentoxide, which separates as a brown precipitate. If a very large excess of acid has been added, the pentoxide passes into solution again as a cation.

The yellow hexavanadate ions, $HV_6O_{17}^{'''}$, are not permanent in the presence either of hydrogen or hydroxyl ions, and the rate of their disappearance corresponds with the velocity of a reaction of the first order.

In contrast to the phosphates, the change of metavanadate into pyro- and ortho-vanadate takes place instantaneously. J. C. P.

Radioactive Constituents of the Bismuth obtained from Pitchblende from Joachimsthal. WILHELM MARCKWALD (*Ber.*, 1903, 36, 2662—2667).—The "radiotellurium" obtained from Joachimsthal pitchblende (this vol., ii, 81) loses its activity when precipitated from a solution of its chloride by hydrazine hydrochloride, and is then identical with ordinary tellurium; from the filtrate obtained, stannous chloride precipitates a trace of a dark coloured, strongly active substance, but the solution still contains a small quantity of active material which is not deposited on a strip of bismuth until a few drops of bromine have been added to oxidise the stannous

chloride and convert the active metal into bromide. The active substance is easily soluble in nitric acid, and on evaporating with hydrochloric acid, a solution of the chloride is obtained, from which the active metal can be precipitated on a sheet of copper, tin, or antimony.

The remainder of the paper is a discussion of the nature of polonium. When bismuth is dipped into a solution containing radium, as stated by Giesel (this vol., ii, 603), the metal becomes radioactive, but the activity is not in the least comparable with that of "radiotellurium," and the solution is not at all exhausted. Moreover, tellurium precipitated by stannous chloride from a solution of tellurous acid containing radium chloride, although somewhat active, gives, when converted into chloride, a liquid which fails to render active a copper strip immersed in it; in this respect, the "induced" activity is totally different for the activity of "radiotellurium." W. A. D.

Perniobic Acid. PETR G. MELIKOFF and PAUL KAZANETZKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 457—460. Compare Abstr., 1899, ii, 491).—Colloidal perniobic acid may be prepared by acidifying a solution of potassium perniobate, $K_4Nb_2O_{11} + 3H_2O$, with sulphuric acid or by the action of hydrogen peroxide on the hydrate of niobic acid, the solution in either case being dialysed.

Perniobic acid exists both as a hydrosol and as a hydrogel, the former of which gradually decomposes with evolution of oxygen; under the influence of contact, for example, of finely-divided platinum, the decomposition proceeds much more energetically.

By the action of concentrated sulphuric acid on the hydrosol, hydrogen peroxide is not formed, but oxygen is evolved, showing that perniobic acid cannot be represented as a salt of hydrogen peroxide.

T. H. P.

Mineralogical Chemistry.

Gadolinite from West Australia. BERNARD F. DAVIS (*J. Roy. Soc. New South Wales*, 1903 (for 1902), 36, 286—289).—Large, black masses of gadolinite were found with cassiterite, monazite and two varieties of a euxenite-like mineral in veins in gneiss, at Cooglegong in the Pilbarra district. Thin splinters of the mineral are transparent and grass-green, feebly birefringent and with distinct pleochroism. Sp. gr. 4.14. Analysis gave:

SiO ₂ .	FeO.	BeO.	Ce ₂ O ₃ .	(La, Di) ₂ O ₃ .	Y ₂ O ₃ .	MgO.	Loss on ignition.	Total.
23.33	10.38	12.28	2.50	18.30	33.40	0.69	0.32	101.20

When heated, the mineral gives off carbon dioxide, hydrogen, a little nitrogen, and a trace of helium.

L. J. S.

Chrysocolla and Vanadinite in the Copper Mines of Bena (de) Padru, near Ozieri [Sardinia]. DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 81—87).—The author describes a specimen of chrysocolla, which was found mixed with chalcocite, erubescite, chalcopyrite, malachite, and azurite, and which has a hardness of about 3.5 and a sp. gr. 2.4 at 23.3°. An analysis by CARLO RIMATORI gave the following results:

SiO₂, 36.43; CuO, 39.65; Al₂O₃, 3.22; Fe₂O₃ and PbO, traces; CaO, 1.34; H₂O, 19.50. Total, 100.14.

A sample of vanadinite, previously unknown in Sardinia, is also described; it has a hardness of about 3 and a sp. gr. 6.78 at 22.2°, but its composition was not determined.

T. H. P.

Physiological Chemistry.

Analyses of the Gases of the Blood at Different Barometric Pressures. ANGELO MOSSO and GIACOMO MARRO (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 460—465).—The analysis of the gases of the blood should be carried out very quickly after the blood is drawn owing to the changes which the gases undergo.

The authors have modified the apparatus and method given by Barcroft and Haldane (*Abstr.*, 1902, ii, 424) in such a way that the animal need not be kept tied up longer than 5 minutes for each experiment, and that several experiments can be carried out on the same animal in the same day without taking out of action any of the arteries, and only requiring 1 c.c. of blood for each examination. Also, the oxygen is liberated from the sample about 15 or 20 minutes after it is drawn, so that very little change can take place in the composition of the gases.

T. H. P.

Changes Occurring in the Gases of the Blood on the Summit of Monte Rosa. ANGELO MOSSO and GIACOMO MARRO (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 466—477).—By means of the method mentioned in the preceding abstract, the authors have made analyses of the blood-gases of rabbits and dogs at various altitudes up to 4560 metres, the animals being kept for a day in each new locality before being experimented on. In all cases, the blood was drawn while the animal was fasting, and the analysis was carried out immediately. Control experiments were also made under different atmospheric pressures in Turin, which has an altitude of 276 metres.

The results show clearly that under diminished pressure a considerable decrease takes place in the amount of oxygen and carbon dioxide in the blood. The numbers obtained were not constant, and were found to depend on the conditions of nutrition, &c., but successive experiments on the same animal under constant conditions gave very

concordant results. On an average, the amounts of oxygen and carbon dioxide at 430 mm. pressure were only 81.21 and 85.4 per cent. respectively of the quantities at a pressure of 740 mm. T. H. P.

Formation of Sugar in the Blood as it passes through the Lung. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1903, 137, 475—478).—The blood, in circulating through the lung, not only undergoes glycolysis, but, in addition, sugar is formed. This glycogenic function, not hitherto recognised, usually exceeds the opposite change under normal conditions. W. D. H.

Action of Laked Blood. O. LANGENDORFF (*Pflüger's Archiv*, 1903, 99, 30—32).—Laked blood perfused through a frog's heart will not keep it beating. This has been explained by the poisonous action of the potassium salts liberated when the red corpuscles are dissolved. Whether any other alkaloid-like poison is liberated is unknown. The present paper is mainly polemical regarding this point, which has also been taken up by Kronecker and his pupils. W. D. H.

The Laking of Red Corpuscles. HANS KOEPPE (*Pflüger's Archiv*, 1903, 99, 33—91).—Evidence is adduced that the red discs are covered with a semi-permeable membrane. The laking of blood is due to the destruction of this membrane; this may be brought about by the differences of osmotic pressure, as in the action of water. The membrane appears to be, in part at any rate, composed of fatty materials; the solution of this by ether, alcohol, chloroform, and acetone explains the part they play as laking agents. Hydrogen ions produce laking because they catalyse esters, and hydroxyl ions because they produce saponification of esters. Special attention is directed to the influence of temperature on these phenomena. W. D. H.

Concentration of Hydroxyl Ions in Blood-serum. G. FARKAS (*Pflüger's Archiv*, 1903, 98, 551—576).—The hydroxyl concentration of serum at room temperature is from 1×10^{-7} to 3×10^{-7} normal solution. The serum is therefore practically neutral in reaction. The concentration is increased by passing a stream of oxygen through it. W. D. H.

Molecular Concentration of Blood-serum in Pregnancy, and of Amniotic Fluid. G. FARKAS and E. SCIPIADES (*Pflüger's Archiv*, 1903, 98, 577—587).—During pregnancy, the freezing point of the serum rises, and the molecular concentration falls. These values return to the normal after parturition or may slightly exceed it for a time. The electrolyte concentration does not vary, as shown by the conductivity, but the non-electrolytes (excluding proteids) diminish during pregnancy until delivery. Proteids, chlorine, and hydroxyl ion concentration do not change. The results in man are similar to those in other mammals. The amniotic fluid is a hypertonic solution containing traces of proteid, and is not a simple transudation from the blood. W. D. H.

Separation of the Constituents of Blood to which the Decomposition of Hydrogen Peroxide is Due. JULES VILLE and JOSEPH MOITESSIER (*Bull. Soc. chim.*, 1903, [iii], 30, 978—982. Compare this vol., ii, 120, and Cotton, *Abstr.*, 1901, ii, 295).—The authors now show that the decomposition of hydrogen peroxide by defibrinated blood is due in part to the action of hæmoglobin, but principally to an enzyme contained in the stromæ, and which, like hæmoglobin, extravasates from the red corpuscles when the blood is diluted with water. Preparations of the enzyme have been obtained by precipitating calcium phosphate, in presence of excess of calcium chloride, in defibrinated blood previously mixed with nine times its weight of water. From such preparations, solutions of the enzyme can be obtained by treatment with dilute aqueous solutions of ammonium carbonate or citrate, sodium carbonate, disodium hydrogen phosphate, or acetic acid; and from the solutions in acetic acid or ammonium citrate the enzyme itself can be reprecipitated by the addition of alcohol or ammonium sulphate. The activity of the enzyme, when adhering to calcium phosphate, is not destroyed by heating at 100°, but solutions are no longer active after exposure to a temperature of 70° for 1 hour. Solutions of the enzymes pass through Chamberland filters, but the first portion of the filtrate is inactive owing to the adhesion of the enzyme to the walls of the porous cylinder. Preparations of the enzyme have been obtained from the blood of the horse, cow, sheep, and dog. Blood-serum does not decompose hydrogen peroxide, and the liquid expressed from lymphatic ganglia exerts a much less powerful action on hydrogen peroxide than does defibrinated blood.

T. A. H.

Parthenogenesis produced by Carbon Dioxide. YVES DELAGE (*Compt. rend.*, 1903, 137, 449—451, 473—475).—By the action of carbon dioxide, experimental parthenogenesis can be produced in starfish eggs, and the larvæ, which are perfectly formed, lived for six weeks. It is necessary to employ ~~this~~ reagent after the emission of the polar globules. Similar results were obtained with other echinoderms.

W. D. H.

Artificial Parthenogenesis. JACQUES LOEB (*Univ. California Publ. Physiol.*, 1903, 1, 7—9).—A preliminary account of experiments with the eggs of limpets, conducted on the lines of the author's previous work, which shows that these molluscs must be added to the list of animals in which it is possible by physico-chemical means (short immersion in a hypertonic solution) to cause the unfertilised eggs to develop into swimming larvæ. Mechanical agitation has no effect.

W. D. H.

End-products of Auto-digestion of the Pancreas and Yeast. II. FRIEDRICH KUTSCHER and LOHMANN (*Zeit. physiol. Chem.*, 1903, 39, 313—317. Compare this vol., ii, 670).—The end-products obtained by the auto-digestion of yeast are practically identical with those obtained in experiments with the pancreas. Attention is again drawn to the presence of choline. Auto-digestion of the brain,

curiously enough, yields no free choline; the brain tissue evidently contains no enzyme capable of decomposing lecithin; the proteolytic action is also small.

W. D. H.

Influence of the Autolytic Ferment on Pancreatic Digestion. MIECZYSLAW HALPERN (*Zeit. physiol. Chem.*, 1903, 39, 377—389).—Experiments on the liver show that by autolysis alone a considerable amount of proteid matter is digested. The addition of pancreatic ferment assists this action. It is suggested that the greater digestive power of pancreatic extracts on fresh, as compared with cooked, proteids may be due in part to the simultaneous action of autolytic ferments. Details regarding the form in which nitrogen is present in the products of digestion are given.

W. D. H.

Behaviour of Serum towards Tryptic Digestion. CARL OPPENHEIMER and HANS ARON (*Beitr. chem. Physiol. Path.*, 1903, 4, 279—299).—Unaltered serum (especially its globulin constituents) shows a great resistance to tryptic digestion; this is removed or lessened by previous coagulation of the proteids, or previous treatment with pepsin-hydrochloric acid. The action of an antitrypsin will only explain this in part, for heating at 68°, which destroys the antitrypsin, only somewhat lessens the resistance; it is regarded as probable that the unaltered serum proteids have a specific configuration which renders it difficult for the ferment to attack them. Some intermediate substance is necessary to link the ferment to the proteid. The time law of Schütz and Borissow does not hold with certainty for unaltered serum and trypsin.

W. D. H.

Combustion of the Muscular Carbohydrate and the Influence of the Pancreas on it. I. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1903, 39, 336—349).—Experiments on dogs without a pancreas, and also with the cell-free juices of muscle and pancreas, show that for the burning of dextrose in the body the co-operation of two organs, namely, the muscles and the pancreas, is necessary. The combustion is attributed to a ferment in the muscle which is rendered active by an internal secretion from the pancreas. One gram of muscle is able to destroy 5—8 grams of dextrose. This action is inhibited by blood-serum. The action of bacteria was excluded by the use of antiseptics.

W. D. H.

Fate of Proteids introduced through the Alimentary Canal and Otherwise. CARL OPPENHEIMER (*Beitr. chem. Physiol. Path.*, 1903, 4, 263—278).—The trend of much recent work on proteid absorption has been to show that the proteid molecule is broken up in the alimentary canal into simple crystalline products, which are then resynthesised to form the body proteids. On the other hand, there is little doubt that a certain fraction of the proteid is absorbed unchanged even under normal circumstances, and is discoverable in the blood by the "biological test." The amount so absorbed depends on several factors, of which the amount of proteid ingested, the activity of the digestive juices and of the absorbing epithelium are the chief

It cannot be doubted, however, that the unaltered foreign proteid is assimilable; it is only when the amount so taken in is great that it passes into the urine. The present experiments on rabbits show that when foreign proteids (serum from other animals and egg-white) are injected intravenously or intraperitoneally, they are directly utilised, and only small but variable amounts pass into the urine. The amount shows no relationship to precipitin formation.

W. D. H.

Absorption of Proteids. M. ASCOLI and L. VIGANÒ (*Zeit. physiol. Chem.*, 1903, 39, 283—304).—After feeding dogs on egg-white, the lymph became precipitable by blood-serum immunised against this proteid. The result with the blood-serum of these animals is variable. Corresponding results were obtained after feeding the animals on roasted meat.

W. D. H.

Digestibility of Vegetables. A. P. BRYANT and R. D. MILNER (*Amer. J. Physiol.*, 1903, 10, 81—99).—The experiments were made on three healthy young men; the faeces were examined first for a period during which a standard mixed diet was taken, and then for a period of three days, during which a measured amount of certain vegetables (cabbage, potatoes, beets, or apples) was added. Of these, the result was that the amount of cabbage utilisable was lowest. The carbohydrate throughout was well digested and absorbed; the foods mentioned are thus sources of energy; so far as proteid and fat are concerned, they are of little value. Their chief use appears to be to add variety and palatability to the diet. Their bulkiness is also useful in keeping up a healthy activity of the alimentary tract.

W. D. H.

Chemical Investigations on Lymphatic Organs. III. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1903, 4, 362—377. Compare this vol., ii, 664).—The following table contrasts the composition of cells from the thymus and lymph-glands:

	Thymus.	Lymph-glands.
Water	80.41	80.41
Proteids ..	15.52	13.79
Histon nucleinate	3.15	0.69
Nucleo-proteid.....	1.08	1.06
Substances soluble in alcohol.....	2.48	4.76
Ash	1.59	1.05

The substance called histon nucleinate appears to be a purer form of what has been termed nucleo-histon. It contains more phosphorus than the nucleo-proteid. Its decomposition products in both thymus and lymph-glands are histon, para-histon, and nucleic acids. That from the thymus contains more phosphorus. The nucleo-proteid of the thymus contains from 0.9 to 1.2 per cent. of phosphorus; that of the lymph cells 0.83. The two sets of cells are, however, not identical, as shown in the foregoing table. The lymph cells are stated to contain

no fibrin-ferment. The cells of red marrow differ from both the foregoing by containing no histon. Those of the spleen contain only traces. Blood plasma and leucocytes contain no histon; the same is true for exudations and transudations. The cells of a round-celled sarcoma yield a histon nucleinate identical with that obtained from lymph cells.

W. D. H.

Iron in the Animal Body. MAX SCHMEY (*Zeit. physiol. Chem.*, 1903, 39, 215—282).—A large number of estimations of the amount of iron in various tissues, especially the muscular tissues of different animals, are given. In rabbits, the red muscles contain rather more than the pale; in the pig and hen, the opposite is true. Feeding on preparations of iron slightly raises the amount in the muscles. In different animals, the percentage of iron in the dry muscle varies from 0.005 to 0.0289. The numbers obtained are usually less than those given by Katz. In heart muscle, the percentage is higher than in voluntary muscle. The amount in the heart and also in the liver slightly increases with the age of the animal.

W. D. H.

Non-Prevalence of Potassium Salts in the Spleen of Marine Fishes. CARLO U. ZANETTI (*Gazzetta*, 1903, 33, i, 234—236).—In most works on physiology or physiological chemistry, the statement is made that: "The acids of the spleen are generally combined with sodium in the case of terrestrial animals, whilst with marine fishes these acids are united almost exclusively with potassium." The author has analysed the ashes of the spleens of four species of sea-fish, the following numbers representing the percentages of sodium and potassium oxides in the total alkali oxide contained in the spleen:

	Na ₂ O.	K ₂ O.
<i>Xiphias gladius</i>	47.52	4.56
<i>Orcynus thynnus</i>	48.64	3.22
<i>Poliprion cernium</i>	45.14	6.60
<i>Cerna gigas</i>	46.19	4.48

Further, on preparing the so-called crystallised spleen of Platner, the percentages of the alkali oxides are found to be: (1) for *Xiphias gladius*, 49.29 Na₂O and 13.42 K₂O, and (2) for *Orcynus thynnus*, 42.78 Na₂O and 12.63 K₂O.

T. H. P.

Formation and Composition of Fat in Hens. ARTHUR ZAITSCHEK (*Pflüger's Archiv*, 1903, 98, 614—622).—Feeding hens on milk leads to the formation of fat in these animals which approaches butter fat in composition, except that the amount of volatile fatty acids is not affected.

W. D. H.

Formation of Sugar in the Perfused Liver. FRIEDRICH KRAUS, jun. (*Pflüger's Archiv*, 1903, 98, 452—463).—In view of Seegen's statement that the liver forms sugar from the products of proteolysis absorbed from the alimentary canal, experiments were performed in

which the liver was perfused with blood by Freund's apparatus and peptone was added to the blood. No increase of the sugar in the liver was found.

W. D. H.

The Total Glycogen in Dogs. BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1903, 99, 191—242).—Pflüger's method of estimating glycogen was used. Great variations in the total amount of glycogen in dogs occurs with constant and abundant diet of meat and carbohydrate. The lowest value per kilo. of body weight obtained was 7.6, the highest 37.87 grams. For every 100 grams obtained from the liver, amounts varying from 76.2 to 398 grams can be obtained from the rest of the body. The maximum amount of glycogen in the liver was 18.7 per cent. The percentage in muscle varies from 0.72 to 3.72. All other organs contain appreciable amounts.

W. D. H.

Glucosamine and Chitose in the Animal Organism. PROVAN CATHCART (*Zeit. physiol. Chem.*, 1903, 39, 423—433).—A few experiments on rabbits show that glucosamine has no influence on glycogen formation. Chitose itself slightly increases the glycogen in liver and muscles; whether it acts as a 'proteid-sparer' is uncertain.

W. D. H.

Chorionin. K. FARKAS (*Pflüger's Archiv*, 1903, 98, 547—550).—The shell of the silkworm's egg consists mainly of a chitin-like substance called chorionin by Tichomirow; it can be prepared by a method which chiefly depends on its insolubility in gastric juice. Its amount in the fresh eggs is 10.46 per cent., or 29.03 per cent. on the dry substance. It contains C, 49.63, and N, 15.64 per cent., and the energy-value of 1 gram is 5115 calories. The substance is believed to be a source of nutriment and energy to the developing embryo, but this question is still left open.

W. D. H.

Hæmocyanin and Hæmerythrin. RUDOLPH KOBERT (*Pflüger's Archiv*, 1903, 98, 411—433).—The cephalopod *Eledone* was used as the source of hæmocyanin. Decalcification of the blood by means of an oxalate was found to prevent fibrin formation. Oxyhæmocyanin shows no absorption bands. The addition of sodium or potassium hydroxide to hæmocyanin gives a biuret reaction; the copper in the molecule cannot therefore be so closely united as is the iron in hæmoglobin. The blood of *Aphysia limacina* contains no hæmocyanin; that of *Maja verrucosa* does. Hæmocyanin in quite dilute solutions can be precipitated by zinc sulphate or copper sulphate; from the precipitate, hæmocyanin can be recovered unchanged. No evidence of the existence of a compound between hæmocyanin and carbon monoxide was found. Blood containing hæmocyanin acts catalytically on hydrogen peroxide. Crystals of hæmocyanin, illustrations of which are given, can be obtained by a modification of the method usually adopted for obtaining proteid crystals. The injection of hæmocyanin into the blood stream of rabbits is harmless.

Hæmerythrin, the pink colouring matter in the blood of *Sipunculus* and a few other worms, is contained in the blood corpuscles; it contains

1.44 per cent. of iron (Cuénot); this metal is not so firmly united to the proteid as it is in hæmoglobin, but more firmly than the copper in hæmocyannin. Attempts to prepare from it a cyanogen compound, a methæmerythrin, hæmin crystals, hæmochromogen, and hæmatoporphyrin failed. The blood acts catalytically on hydrogen peroxide, but the serum does not. A dilute solution of cyclamin, a typical hæmolytic agent, dissolves the corpuscles. Abrin and ricin taken as examples of agglutinating agents, produce no agglutination, but they decolorise the corpuscles.

W. D. H.

Variation in Cow's Milk in the course of Lactation. A. TRUNZ (*Zeit. physiol. Chem.*, 1903, 39, 390—395).—Analyses are given of the milk of two cows, collected at intervals during the course of lactation. In the later periods, the amount of milk secreted diminishes, but its specific gravity and most of the solids, including the proteids, relatively are increased. The proportion of albumin to casein remains remarkably constant throughout.

W. D. H.

Action of Saline Purgatives. JOHN BRUCE MACCALLUM (*Univ. California Publ. Physiol.*, 1903, 1, 5—6).—Barium chloride, sodium citrate, fluoride, sulphate, tartrate, oxalate, and phosphate act as purgatives when introduced into the intestine or injected subcutaneously or intravenously. The salt first named is the most powerful, and the activity decreases in the salts in the order named. Purgation is due to increase of peristalsis and of secretion. The flow of saliva and urine also increases. The effect is manifested within one minute after intravenous injection, and often 15 minutes after introduction into the intestine; the effect is therefore produced after absorption, and is probably due to action on the central or peripheral nervous system. It is not due to hindrance of absorption from the intestine, as Schmiedeberg thought. The effect is neutralised by the injection of calcium chloride. There is a perfect analogy between these actions and the production and suppression of muscular twitchings and nervous hypersensitiveness by saline solutions. The administration of calcium is therefore rational in those cases of diarrhœa which accompany hysteria and nervous excitability of any sort.

W. D. H.

Relation of the Specific Gravity of Urine to the Solids Present. II. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1903, 25, 871—873. Compare this vol., ii, 520).—Since sodium chloride is not a product of metabolism and is present in urine in very variable quantity, a method has been devised for calculating the amount of solids other than sodium chloride in urine. The quantity of sodium chloride present is first ascertained, and the sp. gr. of a solution of this salt of corresponding strength is deducted from the sp. gr. of the urine. The difference multiplied by $0.271 \times 10,000$ gives the amount of solids other than sodium chloride in grams per litre.

E. G.

Occurrence of Monoamino-acids in the Rabbit's Urine after Phosphorus Poisoning. EMIL ABDERHALDEN and PETER BERGELL (*Zeit. physiol. Chem.*, 1903, 39, 464—466).—Small quantities of amino-

acids can be detected by the use of β -naphthalenesulphonic chloride. In rabbits, after phosphorus poisoning, large quantities of glycine and small quantities of an optically active amino-acid were found in the urine.

W. D. H.

Influence of Protoplasmic Poisons on Tryptic Digestion. RUDOLF KAUFMANN (*Zeit. physiol. Chem.*, 1903, 39, 434—457).—The difference between organised and unorganised ferments, so far as the action on them of antiseptics is concerned, is only a matter of degree. Various antiseptics (toluene, chloroform, thymol, sodium fluoride) were employed; they destroy tryptic activity in time; after 24 hours' action, even strong solutions of trypsin are rendered inactive.

W. D. H.

Nitrogen and Proteid in Fæces. ARTHUR ZAITSCHEK (*Pflüger's Archiv*, 1903, 98, 595—613).—The estimation of nitrogen in fæces must be carried out with the fresh material, for on drying the loss of nitrogen is often considerable, especially in carnivora. The previous addition of acid before drying does not entirely abolish the loss. The nitrogen which is lost is non-proteid. The estimation of proteid in metabolism experiments is necessary. A large number of analyses are given.

W. D. H.

Behaviour of Phenylglycine in the Animal Organism. FRITZ ROSENFELD (*Beitr. chem. Physiol. Path.*, 1903, 4, 379—380).—Phenylglycine in decigram doses acts poisonously on rabbits, producing glycosuria; it behaves, therefore, like an aniline derivative.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation of Milk. HENRY TISSIER and PASCAL GASCHING (*Ann. Inst. Pasteur*, 1903, 17, 540—563).—The authors have isolated from milk about thirteen different organisms, the majority of which are already known. *Enterococcus* decomposes sugars to give *i*-lactic, acetic, formic, and valeric acids with traces of alcohol. It attacks dextrose more readily than it does lactose. *Staphylococcus albus* and *S. citreus* are of rare occurrence. A common variety of *Bacillus coli* was also isolated. *B. faecalis alcaligenes*, owing to its faculty of flourishing in a strongly alkaline medium, plays an important rôle in the putrefaction of milk. *B. acidi paralactici* induces lactic fermentation more readily than either *Enterococcus* or *Bacillus coli*, and it yields chiefly *d*-lactic acid. *Proteus vulgaris* and *P. Zenckeri* occur comparatively rarely in milk. *Bacillus subtilis* and *B. mesentericus* were also obtained. *B. lactopropylbutyricus non liquefaciens* is a new species and is fully described; it promotes the

butyric fermentation. The volatile acids, obtained by its action on dextrose, consist mainly of butyric and propionic acids, whilst the non-volatile acids are *i*-lactic acid and a small quantity of the *d*-isomeride. *B. putrificus coli*, *Oididium lactis*, *Rhizopus nigricans*, and a yeast, which is not definitely characterised, were also isolated.

Under the class of mixed ferments are included those organisms which simultaneously attack proteids and carbohydrates; this class is sub-divided into (a) proteolytic organisms, such as *Staphylococcus*, and (b) peptolytic organisms, such as *Enterococcus*, *Bacillus coli*, *B. acidi paralactici*, and *B. lactopropylbutyricus*. The simple ferments, on the other hand, which confine their action to proteids, are also sub-divided into proteolytic organisms, such as *B. mesentericus*, *B. subtilis*, *B. putrificus*, *Proteus vulgaris*, and into peptolytic organisms, such as *Proteus Zenckeri* and *Bacillus fecalis alcaligenes*.

Milk, obtained from a dairy, usually contains all the micro-organisms necessary for its complete decomposition. The mixed ferments first cause a complex acid fermentation, then the lactic fermentation, and finally a lactic, propionic, and butyric fermentation; milk is simultaneously coagulated by the simple ferments; the moulds destroy the acid products and attack the casein; the proteids are finally attacked by the simple ferments.

A. McK.

Nitrogen-fixing Bacteria. ED. VON FREUDENREICH (*Centr. Bakt. Par.*, 1903, ii, 10, 514—522).—In accordance with the results of Gerlach and Vogel (*Centr. Bakt. Par.*, ii, 8, 669, and 9, 817), it was found that pure cultivations of *Azotobacter chroococcum* assimilate free nitrogen. When grown in nutritive solutions containing dextrose, somewhat more nitrogen is fixed than with mannitol. The growth is, however, much greater in mixed than in pure cultures (compare Beyerinck, this vol., ii, 34). The bacterium seems to be widely distributed in soils and was found at a depth of 50 cm.

The best temperature for cultivating the bacteria is 30°.

N. H. J. M.

Nitrogen-fixing Bacteria. MAX GERLACH and IGNAZ VOGEL (*Centr. Bakt. Par.*, 1903, ii, 10, 636—643).—Bacteria of the *Azotobacter* group cannot exist without calcium and phosphoric acid. Potassium and sodium are not essential, but their presence is favourable both to the growth of the bacteria and to nitrogen-fixation.

Old cultivations of the bacteria lose much of their vigour and become more and more sensitive towards dextrose in large amounts. All attempts to maintain the vigour of the cultivations failed, the greatest amount of nitrogen always being fixed by cultures recently obtained from the soil.

Pure cultivations of *Azotobacter* assimilated much more nitrogen (56.3 mg. per litre in 11 weeks) than when cultivated with yeast ($N = 33.3$ mg.), mould fungus ($N = 22.2$ mg.), and with *Streptothrix* ($N = 22.0$ mg.). The yeast and *Streptothrix* completely failed in absence of *Azotobacter*. The mould fungus showed some growth in absence of *Azotobacter* and produced the cherry-red dye, but the

amount of nitrogen in the culture was so small as to be within the limits of analytical error.

N. H. J. M.

Production of Mannitol by the Ferments of Sour Wine. PIERRE MAZÉ and A. PERRIER (*Ann. Inst. Pasteur*, 1903, 17, 587—598).—The ferment of sour wine has the same physiological properties as Gayon's mannitic ferment. It secretes zymase, a lactic diastase, and probably a third diastase capable of converting sugar into 3 mols. of acetic acid. In presence of levulose, mannitol is formed by the action of the hydrogen liberated from water. Bacteria which liberate hydrogen are incapable of transforming levulose into mannitol. The amylobacteria cultivated in a 10 per cent. solution of invert sugar in presence of calcium carbonate failed to produce mannitol.

N. H. J. M.

Respiration-coefficient of Different Yeasts on Various Nitrogenous Nutritive Media. E. WOSNESSENSKY and E. ELISSÉEFF (*Centr. Bakt. Par.*, 1903, ii, 10, 629—636).—Three yeasts were employed: *Saccharomyces cerevisiæ*, I. Hansen, *Schizosaccharomyces Pombe*, and *Saccharomyces Ludwigii*. The cultures were made in test-tubes, coated inside with a layer of gelatin (containing peptone, minerals, and sucrose), inverted over mercury. The tubes were kept in the dark. From time to time, samples of the gas were removed for analysis, and the amounts of carbon dioxide, oxygen, and nitrogen determined.

It was found that the respiration-coefficients depend on the variety of the yeast and on the nutritive media. In the method of cultivation adopted, the respiration-coefficients were usually high, indicating that, notwithstanding the abundant aëration, alcoholic fermentation had taken place (compare Buchner and Rapp, *Zeit. Biol.*, 1898, 37, 32).

Schizosaccharomyces Pombe, cultivated in ammonium phosphate, gave very low coefficients, which is attributed to the absence of alcoholic fermentation.

N. H. J. M.

Chemistry of Yeast. THEODOR SEDELMAYR (*Chem. Centr.*, 1903, ii, 258; from *Z. Brauwes.*, 26, 381—385 and 397—402).—The lecithin of yeast was shown by analysis to be dipalmitincholecinlecithin. The extreme difficulty with which albumin is separated from lecithin renders it probable that Hoppe-Seyler and Liebermann are correct in believing that lecithin does not occur in yeast in the free state, but as a lecithalbumin.

As regards other substances present, a carbohydrate which showed the α -naphthol reaction (Molisch), and, after inversion, yielded a *d*-osazone, was found. Xanthine bases and amides were not detected, but hypoxanthine and adenine were found.

Ammonium carbonate extracts of yeast yielded coagulable proteids and non-coagulable substances, probably similar to ψ -mucin. The predominating constituent of ordinary yeast extract is the "peptonoid substance."

N. H. J. M.

Bread Fermentation. CARLO PARENTI (*Chem. Centr.*, 1903, ii, 304; from *Bol. chim. farm.*, 1903, 42, 353—357).—Bread fermentation consists essentially in the alcoholic fermentation of the sugar present in the meal (compare Boutroux, *Abstr.*, 1891, 1532). There is, in addition, a conversion of gluten into soluble proteids induced by some ferment, other than yeast, which is present in the meal.

There was no change in the starch and dextrin. N. H. J. M.

Power of Resistance of some Mould Fungi towards Metal Poisons. CARL PULST (*Bied. Centr.*, 1902, 32, 563—565; from *Jahrb. wiss. Bot.*, 37, 205—263, and *Naturwiss. Rundsch.*, 17, No. 35).—Experiments were made on the behaviour of *Mucor mucedo*, *Aspergillus niger*, *Botrytis cinerea*, and *Penicillium glaucum* towards copper, zinc, and nickel sulphates and other salts.

Analysis of *Penicillium* grown in presence of copper sulphate showed that the fresh substance contained 0.05 per cent. of copper. The absence of any poisonous effect may be due to copper being retained by the tissues or by dead cells, or to the formation of insoluble copper compounds with organic matter secreted by the protoplasm.

N. H. J. M.

Formation of Glycogen in Fungi grown in Solutions of Sugar. ÉMILE LAURENT (*Compt. rend.*, 1903, 137, 451—453).—The formation of glycogen in moulds grown in a saline solution containing a small quantity of sugar is much increased by the addition of hydrochloric acid (1 in 1000—2000). By adding a small amount of malto-peptone, growth increases, but the formation of a reserve of glycogen diminishes.

W. D. H.

Intramolecular Respiration of the Sugar Beet. JULIUS STOKLASA, JOHANN JELÍNEK and EUGEN VÍTEK (*Zeit. Zuckerind. Böhm.*, 1903, 27, 633—662).—By a long series of quantitative experiments on the normal and intramolecular respiration of sugar beets under aseptic conditions, it is shown that the amount of carbon dioxide evolved during normal respiration is always about double that given off in intramolecular respiration. With fall of temperature, the evolution of carbon dioxide diminishes. The intensity of the respiration varies considerably with the condition of development of the beet, and with young beet is extraordinarily high, but, as the age increases, the respiration diminishes very considerably. Parallel with the respiration runs the assimilation carried on by the chlorophyll. After all the reserve material in the root has been used up, the respiration is very low and sinks further when the leaves die off. The respiration is most intense in the upper parts of the root, and takes place to a much less extent in the middle and lower portions. The nitrogenous matter and the proteolytic enzyme are distributed in the same way.

The results obtained show clearly that the anaërobic respiration of the sugar beet is a process identical with the alcoholic fermenta-

tion carried out by yeast; carbon dioxide and alcohol are formed, together with smaller proportions of glycerol and succinic acid.

T. H. P.

Disappearance of Reducing Sugar in Sugar-cane. HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1903, 25, 855—857).—The proportion of reducing sugar to sucrose in the juice of the sugar-cane is very high in the early stages of growth, but is gradually reduced to a minimum as the plant approaches maturity. Any deterioration in the plant due to injury or over-ripeness tends to increase again the percentage of reducing sugar at the expense of the sucrose. Four samples of sugar-cane have been recently examined the juice of which contained no reducing sugar. These are the only samples ever analysed by the author in which this phenomenon has been observed.

E. G.

Sucrose in Plants. ÉMILE BOURQUELOT (*J. Pharm. Chim.*, 1903, [vi], 18, 241—248).—The author has concluded his research as to the presence of sucrose in plants by means of the invertin process (Abstr., 1902, ii, 55). A variety of roots, fruits, seeds, barks, grains, &c., has been subjected to the test. As to the result, it may be stated that sucrose is one of the most widely distributed substances in phanerogamic plants.

L. DE K.

Avenine. ST. WEISER (*Pflüger's Archiv*, 1903, 98, 623—630).—Sanson described an alkaloid obtainable from oats, which he termed avenine (Abstr., 1884, 915). In yielding an alkaloid, oats would therefore be exceptional among the *Graminaceae*. Wrampelmeyer (Abstr., 1889, 1223) doubted the correctness of Sanson's results, and the present research shows that oats do not contain any alkaloid. Sanson's avenine was probably a mixture of proteid materials.

W. D. H.

Proteolytic Enzyme of Germinating Barley (Malt). FR. WEISS (*Chem. Centr.*, 1903, ii, 298—299; from *Meddel. Carlsberg Lab.*, 1903, and *Zeit. Ges. Brauwes.*, 26, 301—305; 318—322; 334—338; 352—355; 368—371; 386—389; 403—412; 426—428, and 446—449. Compare Abstr., 1901, ii, 69).—The enzyme peptase which produces albumoses and peptones is active at low temperatures (4°, 20°), but the most suitable temperature is 51°, at which the action is nearly twice as much as at 35° or at 60°. The conversion of albumoses by the second enzyme, tryptase, into substances which are not precipitated by tannic acid is a slower process. Its optimum temperature is 45—50° (probably 47—48°), but at 35° the action is not much slower; at 60°, the action is much retarded, and at 70° it ceases altogether.

Solutions of proteids of low concentration showed the least actual amount, but the greatest percentage, of decomposition products. The greatest action was in solutions containing 3—4 per cent. of proteids.

N. H. J. M.

Fermentative Fat-hydrolysis. KARL BRAUN (*Ber.*, 1903, 36, 3003—3005. Compare this vol., ii, 446).—Abrin from *Abrus precatorius* hydrolyses castor oil seeds only with extreme slowness. Previous heating to 90° entirely destroys the action of the ferment. Crotin has no action on castor oil seeds. E. F. A.

Effect of Sulphurous Acid on Plants and Fishes. JOSEF KÖNIG and J. HASENBÄUMER (*Bied. Centr.*, 1903, 32, 535—536; from *Fähling's landw. Zeit.*, 1902, 853 and 893).—Sulphurous acid and calcium hydrogen sulphite increased the total ash of plants and the percentages of potassium, calcium, and sulphuric acid in the ash. The same effect has been observed when plants have been exposed to air containing sulphur dioxide.

In water-cultures, 50 mg. of sulphurous acid or calcium hydrogen sulphite per litre killed the plants in a short time.

A carp weighing 195 grams and a tench weighing 48 grams were not injured by 17.5 mg. of calcium sulphite per litre; but 20—30 mg. of free acid and 30—50 mg. of calcium hydrogen sulphite are injurious. Goldfish are somewhat less sensitive. N. H. J. M.

Experiments on Peas in Water Culture. JOHN GOLDING (*Centr. Bakt. Par.*, 1903, ii, 11, 1—7).—Peas were grown in non-nitrogenous solutions under the following conditions: (1) the roots were completely covered with water; (2) air was further excluded by a layer of oil on the water; (3) part of the roots, with nodules, were exposed to air; (4 and 5) the roots were completely covered, air and oxygen respectively being passed through the solution. The solutions were inoculated by means of extracts of pea-nodules.

No fixation of nitrogen took place when access of nitrogen and oxygen to the roots was prevented by a layer of oil on the surface of the water. In absence of oil, some assimilation took place, but this may have been due to the difficulty of keeping the surface nodules always submerged.

The growth of the plants, which depended on nitrogen assimilation was much less than in presence of combined nitrogen. In sand cultures, inoculated plants produced as much, or more, growth than when supplied with combined nitrogen, but without inoculation.

N. H. J. M.

Ash Constituents of Potato Leaves at Different Periods of Growth and under Different Manurial Conditions. JOSEF SESSL (*Chem. Centr.*, 1903, ii, 56—57; from *Zeit. landw. Versuchswes. Oesterr.*, 6, 537—554).—Kainite and superphosphate raised, directly or indirectly, the percentages of calcium and magnesium. The greatest amounts of phosphoric acid were found at the flowering period, or immediately afterwards, whilst the other constituents did not reach their maximum until later. The relation between potassium and phosphoric acid was frequently 1 : 3 to 1 : 4, and the relation between magnesium and calcium still more regularly 1 : 2.6—2.9.

N. H. J. M.

Manurial Experiments with Seed Beet. HERMANN BRIEM (*Bied. Centr.*, 1903, 32, 668—670; from *Oesterr.-Ung. Zeit. Rübenzuckerind. u. Landw.*, 32, Heft 1).—Molasses slump (containing N, 3; K_2O , 11; and CaO , 5 per cent.) may be utilised to economise sodium nitrate, but cannot replace it entirely. N. H. J. M.

Action of Lime on certain Nitrogenous Substances contained in Beet Juice. EUGÈNE SELLIER (*Zeit. Ver. deut. Zuckerind.*, 1903, 571, 787—798).—From the results of a series of experiments on the action of lime and subsequent saturation with carbon dioxide on beet juice under conditions similar to those obtaining in the practical treatment of the juice, the author concludes that the evolution of ammonia observed is due exclusively to the hydrolysis of the acid amides. The other nitrogenous substances present in the juice undergo change without, however, giving rise to ammonia. Coagulated proteids are not, under ordinary conditions, dissolved again by the action of lime, but by long-continued treatment they are attacked and apparently converted into a soluble form. It is hence recommended to heat the limed juice to about 80° for not longer than 30 minutes. Saturation of the limed juice with carbon dioxide does not purify it from nitrogenous products excepting by removing dissolved ammonia. T. H. P.

Course of Absorption of Phosphoric Acid in Sugar Beet. ACH. GRÉGOIRE (*Chem. Centr.*, 1903, ii, 59—60; from *Bul. Inst. Chim. Bact. Gembloux*, 1903, No. 73, 22—31).—Phosphoric acid was determined at intervals of two weeks by oxidising the dried roots with sulphuric and nitric acids. The greatest assimilation was in August. Very little of the phosphoric acid of the manure (superphosphate) was utilised, the greatest amount being at the commencement of growth, when about one-fifth of the total phosphoric acid absorbed was derived from the manure. Nevertheless, the effect of phosphoric acid manuring on the crops was very considerable, and this is attributed to the small amount of readily available phosphoric acid taken up at the commencement. N. H. J. M.

Nitrogen in Atmospheric Precipitation. B. M. WELBEL (*Bied. Centr.*, 1903, 32, 649—650; from *J. exper. Landw.*, 1903, 4, 194. Compare this vol., ii, 508).—In 1902, the rainfall at Ploty amounted to 410.5 mm. The rain-water contained NH_3 , 1.003; HNO_2 , 0.030; and HNO_3 , 0.253 per million. N. H. J. M.

Dependence of the Amount of Nitrogen as Nitrates on the State of Cultivation of the Soil. R. TRETJAKOFF (*Bied. Centr.*, 1903, 32, 507—512; from *J. exper. Landw.*, 1902, 580—608).—Early ploughing increased the amounts of nitrates in the soil. In dry weather, an application of farmyard manure acted unfavourably, nitrification being diminished and denitrification increased; the manured plot yielded less grain and straw than the unmanured plot.

Leguminous crops increased the total nitrogen of the soil and the nitrogen soluble in water, the increase being chiefly in the form of ammoniacal nitrogen. N. H. J. M.

Action of Phosphoric Acid in Different Phosphates. OSKAR BÖTTCHER (*Bied. Centr.*, 1903, 32, 655—659; from *Illustr. Landw. Zeit.*, 1903, 31 and 32).—The results of pot experiments in which oats were manured with double superphosphate and with new phosphatic manures showed that the value of basic slag should be estimated according to the amount of phosphoric acid soluble in citric acid, and that the Dafert-Reitmair method is unsuitable. N. H. J. M.

Analytical Chemistry.

The Testing and Employment of Normal Sodium Oxalate in Volumetric Analysis. S. P. L. SÖRENSEN (*Zeit. anal. Chem.*, 1903, 42, 512—516).—Since the publication of the previous paper on this subject, a pure oxalate, completely freed from water by drying at 240°, has been placed on the market. The remainder of the paper is a *résumé* of the methods already described (this vol., ii, 684).

M. J. S.

Method for the Detection of Chlorides, Bromides, and Iodides. STANLEY BENEDICT and J. F. SNELL (*J. Amer. Chem. Soc.*, 1903, 25, 809—814).—The following method for the detection of chlorides, bromides, and iodides in presence of one another is recommended as simple, delicate, and trustworthy.

Potassium iodate and acetic acid are added to the neutral solution; a coloration indicates the presence of iodide, which can be confirmed by shaking a portion of the solution with chloroform or carbon disulphide. If iodide is present, a further quantity of potassium iodate is added to the solution and the liberated iodine is expelled by boiling. The whole of the iodine having been thus removed, dilute nitric acid is added; if a coloration is produced, the presence of bromide is indicated and may be confirmed by shaking a portion of the solution with chloroform or carbon disulphide. The solution is boiled until colourless, and potassium iodide is then added. The potassium iodide destroys the excess of iodate, and the excess of iodide is in turn decomposed by the nitric acid. The solution is again boiled until colourless, and is then treated with an equal volume of concentrated nitric acid and a few drops of silver nitrate solution. The production of a white precipitate, insoluble on boiling, indicates the presence of chloride.

If a thiocyanate is present, the test for iodide must be made in a small portion of the solution after the addition of sodium acetate. The main portion of the solution is treated as already described, the thiocyanic and hydriodic acids being both completely oxidised in presence of the acetic acid.

If salts of other acids are present, the solution is acidified with dilute

nitric acid and silver nitrate is added. The precipitate is washed and digested with zinc and dilute sulphuric acid; the resulting solution is neutralised, filtered, and examined by the method already described.

E. G.

Purification and Estimation of Iodine. ABRAHAM GROSS (*J. Amer. Chem. Soc.*, 1903, 25, 987—990).—Stas's method of dissolving iodine in concentrated potassium iodide, precipitating with water, and subsequent drying and sublimation was found to give the purest specimen. The best drying agent was found to be sulphuric acid, although the iodine is not contaminated by drying over calcium chloride.

The purity of the iodine may be ascertained by titration as follows: 2 grams of the sample are placed in a flask with 40 c.c. of water and 4 grams of granulated zinc. When colourless, the liquid is diluted to 500 c.c., and in 50 c.c. of this the iodine is titrated with silver nitrate, using potassium chromate as indicator.

L. DE K.

Preparation of Pure Iodine; Action of Dry Potassium Dichromate on Alkali Bromides. LUCIEN L. DE KONINCK (*Chem. Centr.*, 1903, ii, 523—524; from *Bull. Assoc. belge des. chim.*, 1903, 17, 157—165).—In a previous paper by the author on the preparation of pure iodine (*ibid.*, 17, 15), it was assumed that, unlike the alkali iodides, the bromides were not decomposed by fusion with potassium dichromate, but subsequent experiments have shown such not to be the case. Potassium bromide, when fused with potassium dichromate, loses the greater portion of its bromine. When, however, a certain amount of normal potassium chromate has been added, no reaction takes place. This accounts for the fact that a mixture of much potassium iodide with but little bromide still yields pure iodine, as the normal chromate formed in the reaction prevents the decomposition of the bromide.

L. DE K.

New Method for the Estimation of Sulphuric Acid. R. SILBERBERGER (*Ber.*, 1903, 36, 2755—2762).—The estimation of sulphuric acid by barium chloride involves several sources of error, in which the solubility of barium sulphate in acids approximately compensates the retention of barium chloride by the precipitate. The inaccuracy is greater in presence of iron. These defects are completely avoided by precipitation with an alcoholic solution of strontium chloride. The precipitated strontium sulphate is crystalline, filters and washes readily, and does not retain any chloride, and the filtrate is entirely free from sulphate. The presence of iron or zinc salts has no influence on the purity of the precipitate. The method was tested in its application to the estimation of sulphur in pyrites with favourable results.

C. H. D.

Titration of Sulphuric Acid by Benzidine Hydrochloride. WOLF JOHANNES MÜLLER and KARL DÜRKES (*Zeit. anal. Chem.*, 1903, 42, 477—492).—The principle of this method has already been

described (Abstr., 1902, ii, 425). The authors now describe experiments with more widely varying quantities of sulphuric acid, as well as the conditions necessary for accuracy. The precipitated benzidine sulphate always carries down a little of the hydrochloride; by precipitation at boiling temperature, this is reduced to a minimum. Free sulphuric acid requires to be exactly neutralised before titration, as the acidity of benzidine hydrochloride is not altered by the addition of sulphuric acid. The error due to the solubility of benzidine sulphate can be eliminated by working at an appropriate dilution; 1 gram of sulphuric acid requires a volume of 500 c.c.; 0.05—0.01 gram, 50 c.c. The excess of benzidine solution should be restricted to 10—20 c.c., and the error due to absorption of the hydrochloride is got rid of by standardising the alkali hydroxide with known amounts of sulphates.

M. J. S.

Analysis of Persulphates. DIOSCORIDE VITALI (*Chem. Centr.*, 1903, ii, 312—313; from *Boll. Chim. Farm.*, 42, 273—286, 321—326).—Persulphates may be estimated by boiling the solution with barium chloride and collecting the barium sulphate thus formed. Experiments based on the volumetric estimation of the excess of barium or of the chlorine liberated, gave, however, unsatisfactory results. Good results are also obtained by boiling with excess of standard solution of sodium carbonate, evaporating to dryness, igniting the residue, and finally titrating the excess of alkali.

The author communicates a new process based on the insolubility of strychnine persulphate. The solution is mixed with an excess of strychnine nitrate, and after 24 hours the precipitate is collected on a small weighed filter, washed with as little water as possible, dried at 100°, and weighed. One hundred c.c. of mother liquor retain 0.04 gram of strychnine persulphate.

L. DE K.

Estimation of Persulphates. CHARLES MARIE and L. J. BUNEL (*Bull. Soc. chim.*, 1903, [iii], 30, 930—933. Compare Peters and Moody, Abstr., 1902, ii, 105).—The authors find that the decomposition of an alkali persulphate into the alkali sulphate and sulphuric acid by ebullition of an aqueous solution of the salt, the reaction on which Tarugi bases his method for the estimation of persulphates, does not take place so rapidly as that author states (this vol., ii, 238). They suggest the following method for the estimation of persulphates. From 0.3 to 0.4 gram of the salt is dissolved in 100 c.c. of water and the solution exactly neutralised, using methyl-orange as indicator; 2 c.c. of methyl alcohol are then added, and the liquid is warmed at 70—80° for 5 minutes and finally boiled for 10 minutes. At the end of this time, the liquid is cooled and titrated, using methyl-orange as indicator. In estimating ammonium persulphate by this method, the ammonia is oxidised to nitrogen and water, and it is therefore not necessary to eliminate it first by adding a solution of an alkali hydroxide.

T. A. II.

Quantitative Separation of Selenium from Tellurium. GIOVANNI PELLINI (*Gazzetta*, 1903, 33, i, 515—518. Compare Jannasch and Müller, Abstr., 1899, i, 59).—To a solution of selenium and

tellurium dioxides containing 0.1 to 0.5 gram and made faintly acid with hydrochloric acid, is added from 50 to 100 c.c. of saturated ammonium tartrate solution, after which the liquid is heated for 1 to 2 hours at 50—60° with hydrazine sulphate, which, under these conditions, reduces the selenium, but not the tellurium dioxide. A little hydrazine sulphate should then be added in order to make certain of the total precipitation of the selenium, which is collected on a tared filter or in a Gooch crucible, washed with warm water and a little absolute alcohol, dried at 105°, and weighed as selenium. The tellurium in the filtrate is precipitated by means of hydrogen sulphide, the liquid filtered through a small filter on which the precipitate is washed with water; the filter and precipitate are then treated in a crucible with fuming nitric acid of sp. gr. 1.52 and the excess of acid expelled on the water-bath, the mass being then dissolved in hydrochloric acid and the sulphuric acid formed by the oxidation precipitated by means of barium chloride and filtered off; the tellurium in the filtrate is reduced by hydrazine hydrochloride, filtered off quickly, washed with water, and finally with absolute alcohol, dried at 105°, and weighed.

T. H. P.

Applicability of Dumas's Method to the Estimation of Nitrogen in Gaseous Mixtures. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 411—416).—The author has applied Dumas' method of estimating nitrogen to the case of generator or Dowson gas, where this is the only determination necessary, and also to the direct measurement of nitrogen in an ordinary gas analysis, in which it serves as a check on the other numbers obtained. The apparatus employed is the same as that generally used in this method, except that the carbon dioxide passes into the copper oxide tube by means of one arm of a T-piece, through the other arm of which is passed the gas to be analysed. To be quite certain that no other gas is present in the nitrogen measured, it is best to pass the latter a second time through the copper oxide tube and again measure it. The method gives results in good agreement with those obtained by Hempel's method.

In using the method for technical purposes, it is best to employ an iron tube for the copper oxide and to provide the ends of the tube with cooling arrangements.

T. H. P.

Estimation of the Nitrogen in Creatine by Kjeldahl's Method. CARL BEGER, GUSTAV FINGERLING, and AUGUST MORGEN (*Zeit. physiol. Chem.*, 1903, 39, 329—335. Compare this vol., ii, 687).—The recent statement by Kutscher and Steudel that Kjeldahl's method cannot be employed in the analysis of many substances of physiological importance was supported by experiments in which, in particular, creatine yielded untrustworthy results. The present experiments show that this is unfounded. Kutscher and Steudel's results are explained by their not having applied the Kjeldahl method with proper precautions; in particular, the period of boiling with acid was too short.

W. D. H.

Kjeldahl's Method. HANS MALFATTI (*Zeit. physiol. Chem.*, 1903, 39, 467—472).—Another protest against the objections raised by Kutscher and Steudel (this vol., ii, 687) as to the value of Kjeldahl's method. In the author's experience, even in relation to creatine and creatinine, the method yields trustworthy results. Naturally it would not be employed alone in the estimation of nitrogen in substances of unknown constitution.

W. D. H.

Detection and Estimation of Ammonia by means of Sodium Picrate. C. REICHARD (*Chem. Zeit.*, 1903, 27, 979—980, 1007—1008).—Advantage is taken of the slight solubility of ammonium picrate. The ammonium salt, such as the chloride or sulphate, is dissolved in the smallest possible quantity of cold water, the solution is heated to boiling, and mixed with an excess of a boiling 10 per cent. solution of sodium picrate. The liquid is then allowed to cool gradually, and when quite cold is decanted. The portion adhering to the crystals is removed by means of filter-paper, which operation may be conducted without any loss of substance. The crystals are then dried at 60—70° and weighed. Carbonates or cyanides should be absent, and also compounds of potassium, rubidium, and caesium, but lithium does not interfere.

L. DE K.

Estimation of Nitrates in Waters by the Schultze-Schlœsing Method. LUCIEN L. DE KONINCK (*Chem. Centr.*, 1903, ii, 461—462; from *Bull. Assoc. belge des chim.*, 1903, 17, 117—120).—To estimate a nitrate in the presence of a carbonate by the Schulze-Schlœsing process, the gas evolved by the action of hydrochloric acid and ferrous chloride is collected over aqueous potassium hydroxide, and the resulting nitric oxide is finally measured over water. It is, however, more convenient first to decompose the carbonates. Bromides do not interfere.

When estimating silica in water containing nitrates, the author prefers to acidify with sulphuric acid instead of hydrochloric acid, at least when a platinum dish is used.

L. DE K.

Estimation of Arsenious Oxide in Paris Green. JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1903, 25, 963—968).—A modification of the Avery-Beans method (*Abstr.*, 1901, ii, 623), consisting in determining separately the free undissolved arsenious acid and the portion dissolved by the acid employed.

0.3 to 0.4 gram of the sample of Paris green is treated with strong hydrochloric acid until all the "green" has dissolved, and the undissolved residue is washed and collected. The arsenious acid which has passed into the solution is estimated by the Avery-Beans method. The undissolved portion is boiled with water and 5 grams of sodium hydrogen carbonate, and when cold it is made slightly acid to methyl-orange. It is then again rendered alkaline with sodium hydrogen carbonate and titrated as usual with standard iodine.

L. DE K.

The Mercury Cathode in Electrochemical Analysis. EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1903, 25, 883—892).—The use of a mercury cathode in electrochemical analyses is advantageous. Sulphates of copper, nickel, zinc, and iron completely deposit the metals; iron may thus be separated from uranium, titanium, zirconium, and thorium. The sulphuric acid liberated may afterwards be titrated.

Nitrates may be similarly decomposed. It is found that if sulphuric acid is added, the nitric acid is not reduced to ammonia, but is liberated as such, and may be determined by titration, allowing, of course, for the added sulphuric acid.

Haloids of sodium, barium, &c., may be analysed by using a weighed silver-coated platinum gauze as anode. The chlorine, for instance, combines with the silver, and is estimated from the increase in weight. The metal, sodium for instance, combines with the mercury, and by substituting a platinum spiral and reversing the current it passes again into the water as hydroxide, which may then be titrated.

The use of Drown and McKenna's anode and also of the carbon pencil may be avoided by the following contrivance. A small beaker of 50 c.c. capacity is taken, near the bottom of which there is introduced through the side a thin platinum wire. Internally, this dips into the mercury, whilst externally it touches a disc of sheet-copper on which the beaker rests and which is connected with the negative electrode of a cell, thus making the mercury the cathode. The amalgam obtained is finally washed with alcohol and ether.

L. DE K.

Titration of Metals with Iodic Acid. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 435—444).—The amount of metal in a solution may often be estimated by adding not too small an excess of potassium iodate solution (suitably of about 2 per cent. strength), diluting to a known volume, allowing to remain for a time, filtering from the precipitate of iodate, mixing an aliquot part of the liquid with dilute sulphuric acid and potassium iodide, and titrating the liberated iodine with *N*/10 thiosulphate solution and starch as indicator. The iodate solution itself is also standardised with the *N*/10 thiosulphate. In the case of barium and lead salts, five minutes to half an hour suffice for the digestion, and the solution should contain free acetic acid; any free mineral acid present should be removed by adding sodium acetate. With mercuric salts, some nitric or sulphuric acid should be present, but not hydrochloric acid; the digestion should be continued for one day in a cool place. With mercurous and silver salts, free nitric or sulphuric acid should be present, and the digestion should be continued for two hours and for five minutes respectively. With bismuth salts, the precipitate had a very varying composition, and consequently bismuth cannot be estimated in this way. Of the *N*/10 thiosulphate solution, 1 c.c. = 0.001145 gram Ba, 0.00172 gram Pb, 0.001669 gram Hg^{''}, 0.003338 gram Hg['], and 0.001798 gram Ag.

Iodic acid may be estimated in a similar manner by adding a known excess of standard silver sulphate solution, then an excess of iodate solution, allowing to remain, filtering, and titrating with thiosulphate;

1 c.c. of *N*/10 thiosulphate solution = 0.01749 gram IO_3 . Silver nitrate cannot be used, as some of the excess of it is carried down by the precipitated silver iodate. C. F. B.

Rapid Precipitation of Metals in the Electrolytic Way. FRANZ F. EXNER (*J. Amer. Chem. Soc.*, 1903, 25, 896—907).—An ordinary platinum dish is used as cathode, the anode being a spiral 2 inches in diameter of heavy platinum wire; its centre is depressed to give it the form of a shallow bowl. It should be made to perform 500—600 revolutions per minute. The volume of the liquid should not exceed 125 c.c. It is heated to boiling at the start, but no further heating is necessary during the electrolysis. That under these circumstances the metals are rapidly and completely precipitated from suitable solutions was proved by a large number of experiments.

L. DE K.

Electrolytic Separations of Metals. EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1903, 25, 892—896).—Silver may be separated by electrolysis from selenium, both in the presence of potassium cyanide or free nitric acid. Mercury may be similarly separated from selenium. Both silver and mercury may be separated from tellurium in the presence of nitric acid, but not of potassium cyanide. Copper may be separated from selenium both in the presence of potassium cyanide and free nitric or sulphuric acid. From tellurium, it may be separated in the presence of free nitric acid, but not of potassium cyanide. Full details are given of the strength of the currents, &c.

L. DE K.

Colorimetric Estimation of Small Quantities of Potassium. LUCIAN A. HILL (*J. Amer. Chem. Soc.*, 1903, 25, 990—992).—The potassium platinichloride precipitate, obtained in the usual manner, is dissolved in boiling water and diluted to a definite volume of say 100—200 c.c. Fifty c.c. of this solution are placed in a colour comparison cylinder and 3 c.c. of stannous chloride solution added. By comparing the yellow colour thus produced with that obtained from solutions of known strength, the amount of potassium may be readily ascertained.

The stannous chloride solution is prepared by boiling 75 grams of granulated tin with 400 c.c. of hydrochloric acid until nearly all dissolved. The standard comparison liquid is made by dissolving 0.518 gram of potassium platinichloride in 100 c.c. of water; before use, 1 c.c. of this is diluted to 100 c.c., when each c.c. will represent 0.01 mg. of potassium oxide.

L. DE K.

Volumetric Estimation of Sodium Sulphide. MARTIN BATTEGAY (*Zeit. Farb.-Text. Chem.*, 1903, 2, 349—350).—To a suitable volume of the sodium sulphide solution, the alkali of which has been exactly neutralised with acetic acid, using phenolphthalein as indicator, a solution of zinc sulphate of known strength is added until the whole of the sulphur of the sodium sulphide is precipitated as insoluble zinc sulphide; the end-point is reached when, on placing a drop of the solution on blotting-paper moistened with cadmium sulphate, a yellow coloration of cadmium sulphide is no longer produced.

The sodium sulphide can also be estimated in the solution by titrating the sulphide and thiosulphate together, after neutralising the alkali with acetic acid, by means of a *N*/10 iodine, and subsequently determining the amount of thiosulphate left in solution after precipitating the sulphide with an excess of zinc sulphate. A series of analyses are quoted, showing the close concordance of results obtained by the two methods.

W. A. D.

Rapid Gravimetric Method of Estimating Calcium. FREDERICK B. GUTHRIE and C. R. BARKER (*J. Roy. Soc. N. S. Wales*, 1902, 36, 132—134).—The following method for the estimation of calcium is recommended as being both rapid and accurate. The calcium oxalate is precipitated, washed, and dried in the usual way, and transferred to a platinum crucible. Ammonium nitrate, previously dried at 100° and powdered, is mixed with the calcium oxalate in the proportion of about 3 of the former to 2 of the latter. The crucible is then heated cautiously with the Bunsen flame for 10 minutes. The whole of the calcium salt is thus converted into oxide, and further ignition by means of the blowpipe is unnecessary.

E. G.

Evaluation of Commercial Calcium Carbide. VINCENZO RECCHI (*Gazzetta*, 1903, 33, i, 153—155).—The author describes a simple apparatus for determining the volume of acetylene evolved by a sample of calcium carbide. It consists of two Marriotte's bottles, the lower apertures of which are connected by a piece of india-rubber tubing furnished with a clip. One of the bottles, A, has a mark on its neck up to which it is filled with water saturated either with salt or acetylene; into the mouth of A is fitted, by means of an india-rubber stopper, a piece of wide glass tubing 10 cm. long, which is closed at its upper end by an india-rubber stopper, through which passes a glass rod, carrying at its lower extremity a small cylindrical metal box holding a known weight of the carbide. The other bottle is lowered, the clip on the connecting tube loosened, and the carbide lowered into the water. When all action ceases, the liquids in the two bottles are brought to the same height, the clip closed, and the bottle A then filled up to the mark on the neck from a graduated vessel. The volume of water added equals that of the acetylene generated.

Using bottles of 3 litres capacity, as much as 15 grams of the carbide may be taken, so that the use of a fair average sample may be ensured.

T. H. P.

Detection of Strontium in the presence of Calcium by means of Potassium Chromate and Ammonia. C. REICHARD (*Chem. Zeit.*, 1903, 27, 877—879, 895—896, 913—914).—Calcium salts are not precipitated by potassium chromate unless the solutions are exceedingly concentrated; the precipitate is then pale yellow and crystalline, but only represents a portion of the calcium. On adding ammonia, strong solutions of calcium are slightly precipitated by potassium chromate. The calcium precipitate does not adhere to the sides of the beaker, which distinguishes it from the strontium precipitate. Strontium salts in dilute (1.5 to 2 per cent.) solutions are

precipitated by potassium chromate, and on adding ammonia even more dilute solutions are affected. The precipitate looks almost exactly like the yellow molybdate precipitate. If strontium is to be looked for in the presence of calcium, the use of ammonia should be avoided. The liquid should be heated to 70° or 80°, but not be raised to boiling; the characteristic deposit of strontium chromate will then strongly adhere to the sides of the vessel.

L. DE K.

Apparatus for the Gasometric Evaluation of Zinc Dust and Similar Work. LUCIEN L. DE KONINCK (*Chem. Centr.*, 1903, ii, 521—522; from *Bull. Assoc. belge des Chim.*, 1903, 17, 112—117).—A specially modified generating flask, which is connected by a spiral vessel (to give elasticity, and, if needed, serve as a condenser) to a gas burette.

L. DE K.

Decomposition of Galena and Chalcopyrite for Analysis. CHARLES BOUCHER (*Bull. Soc. chim.*, 1903, [iii], 30, 933—936).—From 1 to 2 grams of galena in fine powder are mixed with from 4 to 5 times its weight of a mixture of sodium persulphate (3 parts) with ammonium nitrate (1 part) and the mixture heated on a fairly warm sand-bath for 5 or 6 minutes or until no dark particles of undecomposed galena remain. The fused mass is then treated in the usual way.

The procedure with chalcopyrite is similar, but it is recommended to conduct the operation in a matrass of Jena glass to avoid loss by spitting. If the minerals contain manganese, this will be found in the insoluble residue as manganese dioxide. This process is not suitable for the estimation of sulphur in these minerals, and does not give satisfactory results with natural sulphides other than those mentioned above.

T. A. H.

Volumetric Determination of Copper by means of Potassium Xanthate. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1903, [v], 12, i, 435—439).—The method for estimating copper proposed by the author makes use of a decinormal solution of potassium xanthate, which reacts with a copper salt giving a brownish-black precipitate of the formula $(\text{OEt}\cdot\text{CS}\cdot\text{S})_2\text{Cu}$, and this instantaneously decomposes yielding the flocculent yellow compound, $\text{SCu}\cdot\text{CS}\cdot\text{OEt}$. As indicator, *s*-diphenylcarbazide is employed, which with copper salts gives copper diphenylcarbazone, having an intense violet colour (see Cazeneuve, *Abstr.*, 1900, i, 465, and 1900, ii, 627); in presence of the yellow copper compound, the colour will appear brick-red.

The decinormal potassium xanthate is unstable, and must be standardised by titration with copper sulphate solution in presence of *s*-diphenylcarbazide.

The method is carried out as follows: to the copper solution to be tested, an excess of the decinormal potassium xanthate solution is added, then a little diphenylcarbazide solution; the excess of xanthate is then determined by running in standard copper sulphate solution until the brick-red colour appears. About 2 c.c. of a cold saturated 85 per cent. alcoholic solution of *s*-diphenylcarbazide are required for every 0.2 or 0.3 gram of the copper salt.

Good results are obtained by this method, which can be carried out in artificial light as well as, if not better than, in daylight. T. H. P.

Volumetric Estimation of Mercurous Salts and of Mercurous and Mercuric Salts together. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 444—446).—Mercurous salts can be estimated by dissolving a suitable quantity in 10 c.c. of water, adding 10 c.c. of concentrated nitric acid, digesting for half an hour in the water-bath in a bottle with the stopper tied down, aspirating air through the liquid for half an hour in order to remove oxides of nitrogen, adding 2 c.c. of a saturated, or 5 c.c. of a 10 per cent., solution of ferric alum as indicator, and titrating with $N/10$ thiocyanate solution, 1 c.c. of which = 0.010015 gram of mercury (compare Abstr., 1902, ii, 475).

The total mercury in a substance containing both mercurous and mercuric salts can be estimated in the same way. Another titration can be made by the iodate method (this vol., ii, 755). The mercury found in the second titration, reckoned as being all in the mercurous state, will appear greater than in the first titration, because in reality some of it is present in the mercuric state, in which state the same weight of mercury is twice as efficient in its power of precipitating the iodate solution. The apparent excess serves as a measure of the amount present in the mercuric state; that present in the mercurous state can be calculated by difference. C. F. B.

Titration of Hydrargyrum Praecipitatum Alb. ERWIN RUPP (*Arch. Pharm.*, 1903, 241, 447—448).—Of the sample under examination, 0.2 gram is heated for 5 minutes with 25 c.c. of 25 per cent. nitric acid in a loosely closed flask; to the solution so obtained, 10 c.c. of $N/10$ silver nitrate solution are added, followed by 5 c.c. of water; the heating is continued for 10 minutes; the whole is then cooled, mixed with 5 c.c. of 10 per cent. ferric alum solution, and titrated with $N/10$ thiocyanate solution; of this, 17.7 to 18.0 c.c. should be required. Presence of mercuric chloride or of ammonium chloride would make the percentage of chlorine in the sample greater than that corresponding with pure mercurous chloride, and, in consequence, less thiocyanate solution would be required in the titration. C. F. B.

Technical Estimation of Mercury in Poor Cinnabar Ores by Personne's Method. CARLO MONTANARI (*Gazzetta*, 1903, 33, i, 155—160).—Although Personne's method for determining mercury in cinnabar ores gives high results, yet the author considers it the best for technical purposes. For use with ores containing 1 per cent. or less of mercury, an apparatus has been devised to prevent any loss during the action of the aqua regia. This action is carried out in a flask fitted with a ground stopper carrying a vertical glass tube $1\frac{1}{2}$ metres high, and bent over at the top into the form of a hook, the lower end of which is blown into a bulb which tapers at the bottom; the tapering portion dips into water contained in a test-tube carried by a wire twisted round the vertical glass tube. The details of the method are given. T. H. P.

Standardisation of Permanganate. ALEXANDER CLASSEN (*Zeit. anal. Chem.*, 1903, 42, 516—518).—With reference to Skrabal's statement (this vol., ii, 684), that iron prepared by Classen's electrolytic

method from the oxalate is never free from carbon, it is shown that this was due in his experiments to the prolongation of the electrolysis during the night. Even at tensions of 7—8 volts, perfectly pure iron is obtained if the electrolysis is interrupted at the proper time. The carbon is due to the reduction of ammonium carbonate, and is never obtained when oxalic acid is present in the electrolyte. M. J. S.

Electrolytic Separation of Iron and Manganese. J. KÖSTER (*Ber.*, 1903, 36, 2716—2719).—The double ammonium oxalates of iron and manganese, to which an excess of ammonium oxalate is added, are electrolysed with a current of 1.5—2 amperes and 3—4 volts, the time taken being 5—8 hours, and the solution being kept cool. As soon as the separation of manganese dioxide at the anode begins, a small amount of phosphorous acid solution is added, and this treatment is repeated from time to time during the first two hours of the electrolysis. A. McK.

Estimation of Manganese in the Presence of Iron. GEORG VON KNORRE (*Zeit. angew. Chem.*, 1903, 16, 905—911).—A modification of the author's persulphate process (*Abstr.*, 1902, ii, 108). The new process may be employed in the presence of small quantities of nickel, copper, and phosphoric acid.

The sample of iron or steel is, as usual, dissolved in dilute sulphuric acid, oxidised with nitric acid, and the somewhat neutralised solution is boiled with excess of ammonium persulphate. It is now of the greatest importance to remove the excess of persulphate, and this may be effected by acidifying and strongly diluting the solution and then boiling for at least 20 minutes. When cold, the precipitated manganese peroxide is at once dissolved (without previous filtering) by means of a not too large amount of a standard solution of hydrogen peroxide, and the excess of this is then without delay titrated with standard permanganate. L. DE K.

The Accuracy of the Acetate Method for the Separation of Iron and Manganese. ALWIN MITTASCH (*Zeit. anal. Chem.*, 1903, 42, 492—509).—The discordant opinions of various operators as to the separation of iron and manganese by the acetate method are undoubtedly due to the indefinite mode of conducting the precipitation. For a successful separation by a single precipitation, it is necessary that the free acetic acid and the alkali acetate should be present in approximately molecular proportions. The solution must be acid, but with acetic acid only. Filtration proceeds most rapidly if the acetate is not added until the solution has been heated nearly to ebullition, but the preliminary neutralisation of the solution should take place in the cold; a very short boiling (1 minute) is quite sufficient.

Either ammonium or sodium acetate may be used, but as commercial ammonium acetate is generally strongly acid, this must be allowed for in apportioning the amount of free acid to be added. It is not necessary to add either acetic acid or an acetate to the water employed for washing the iron precipitate. The quantity of acetate

used may be varied within somewhat wide limits, and if the above conditions are carefully adhered to the precipitation of the iron is absolutely complete, and not a trace of manganese can be detected in the precipitate.

M. J. S.

Analysis of Chromic Acid and of its Ammonium Salts. DIMITRI DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 408—411).—When ammonium salts of chromic and dichromic acids are heated, they decompose, leaving only a residue of chromium trioxide, and the author employs this method for determining the percentage of chromium present in these salts. The heating is carried out in a Jena glass flask closed with a glass wool plug. The method gives results concordant with one another and with those obtained iodometrically.

T. H. P.

Reduction of Molybdic Acid by Zinc; Ratio of Bismuth to Molybdenum in Bismuth Ammonium Molybdate. EDMUND H. MILLER and HENRY FRANK (*J. Amer. Chem. Soc.*, 1903, 25, 919—928).—The authors confirm the statement of Riederer (see this vol., ii, 762) that the ratio of molybdenum to bismuth in bismuth ammonium molybdate is as 2 : 1.

A series of experiments has been made to ascertain the exact reducing power of zinc on molybdic acid in the presence of sulphuric acid. Under normal conditions, the compound finally obtained closely corresponds with the formula $\text{Mo}_{24}\text{O}_{37}$.

L. DE K.

Estimation of Uranium and Uranyl Phosphate by the Zinc Reductor. O. S. PULMAN, jun. (*Amer. J. Sci.*, 1903, 16, 229—239).—A standard solution of uranium nitrate is converted into a solution of uranium sulphate; the latter is reduced by amalgamated zinc and the resulting uranous salt titrated with standard potassium permanganate (compare Kern, *Abstr.*, 1902, ii, 51). The results were high when carbon dioxide was passed during the reduction into the flask containing the reduced product, but sharp results were obtained when no carbon dioxide was present and when the titration was performed in presence of air. It is accordingly supposed that the uranium salt is reduced by the zinc reductor below the uranous stage and then reoxidised by the atmosphere; the lower oxide is rapidly oxidised under those conditions to exactly the uranous state, whilst the uranous salts are sufficiently stable to permit of their being estimated before they are oxidised.

A. McK.

Estimation of Vanadium. ÉMILE CAMPAGNE (*Ber.*, 1903, 36, 3164—3176).—Vanadic acid or its salts are reduced by evaporating nearly to dryness with much concentrated hydrochloric acid, the operation being repeated three times. Finally, a small quantity of sulphuric acid is added and the heating continued until all hydrogen chloride has been driven off. The residue is taken up in about 300 c.c. of water, heated to 60°, and titrated with permanganate.

In applying the method to steel analysis, the metal is dissolved in nitric acid and the nitrates converted into oxides by gentle ignition. These

are dissolved in concentrated hydrochloric acid and boiled with ferric chloride, converting the oxychloride, VOCl_3 , present into VOCl_2 . Most of the iron is removed by Rothe's method, namely, extraction with ether; the aqueous solution is then again boiled with hydrochloric acid and the chlorides converted into sulphates, when ferric sulphate and divanadyl sulphate are formed; the latter is directly titrated with permanganate.

E. F. A.

Volumetric Estimation of Bismuth as Molybdate and its Separation from Copper. HERMAN S. RIEDERER (*J. Amer. Chem. Soc.*, 1903, 25, 907—919).—*Volumetric Estimation of Bismuth.*—The nitric acid solution of bismuth is mixed with a large excess of ordinary molybdate solution, and the free nitric acid is then nearly neutralised with ammonia, using methyl-orange as a guide. After warming for some time, the precipitate is collected and washed with a 3 per cent. solution of ammonium sulphate. It is then dissolved in dilute sulphuric acid and treated in a reductor with zinc, and the resulting molybdenum oxide is titrated as usual with standard permanganate. Provided the precipitate is of a pure white colour, the ratio between molybdenum and bismuth is practically as 2:1.

Separation of Bismuth from Copper.—The solution is mixed with a large excess of tartaric acid and then rendered strongly alkaline with potassium hydroxide. Potassium cyanide is now added until the blue copper colour has disappeared, and the bismuth is then precipitated with hydrogen sulphide. This is then well washed and redissolved in dilute nitric acid, from which solution it is then precipitated as carbonate or else it is titrated as first directed.

L. DE K.

Gas Burner. L. QUENNESSEN (*Bull. Soc. chim.*, 1903, [iii], 30, 998—999).—This burner has been devised to facilitate the treatment with strong acids of the metallic "cornets" obtained in the assay of gold, silver, and platinum. It consists of a Bunsen burner, in which the rose takes the form of an expanded tubular ring perforated on its inner surface; the top of the burner tube is fitted with an adjustable rest of special pattern, on which the glass tube containing the cornet and the appropriate acid stands, and is further supported by a wire rest rising from a clamp, attached half-way down the burner tube. By this means, the glass tube is heated laterally, with the result that "spirting" of the liquid is prevented, and the risk of fracture of the tube or breakage of the cornet is minimised. The burner is figured in the original.

T. A. H.

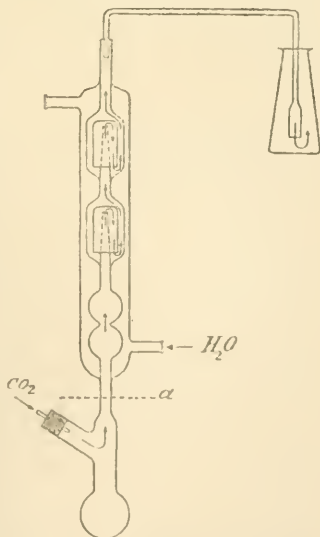
Analysis of India-rubber and Rubber Goods. CARL O. WEBER (*Ber.*, 1903, 36, 3103—3108. Compare Abstr., 1902, i, 553; Harries, Abstr., 1902, i, 811; this vol., i, 189, 642).—The nitric peroxide from 20 grams of lead nitrate is passed through a tower containing phosphoric acid and then led into a benzene solution of the crude rubber until the solution has a reddish-brown colour. The mixture is left for an hour and the yellow solid, $\text{C}_{10}\text{H}_{16}\text{O}_4\text{N}_2$, removed, dried at 50° , and dissolved in acetone, when mineral impurities are left behind. The clear solution is poured into water and the precipitated compound filtered

on a tared filter paper and dried at 90° . Resin is removed by extraction with acetone before the rubber is treated with the nitric peroxide.

Vulcanised rubber is first extracted with acetone, and oils, paraffins, resins, and sulphur estimated in this extract in the usual manner. The residue is dried in an atmosphere of coal gas, weighed, and extracted twice with normal alcoholic soda; it is then washed with hot water, dried in a current of coal gas, weighed, and the solution in dry benzene treated with nitric peroxide and the subsequent operations conducted as just described. If the acetone solution of the additive compound is poured into water, a yellow oil is obtained, which solidifies only slowly. This difficulty may be overcome by pouring the acetone solution into a 10 per cent. aqueous solution of ammonium chloride, when a solid precipitate is obtained. This has not the simple composition $C_{10}H_{16}O_4N_2$, but contains sulphur and often chlorine. The sulphur may be estimated by oxidation in an open vessel with concentrated nitric acid, evaporation to dryness, first alone and then with saturated sodium acetate solution, and final oxidation by fusion with a small amount of potassium nitrate. The chlorine may be estimated by the Carius method.

The percentage of sulphur or of sulphur and chlorine calculated on the amount of pure rubber present is termed the "coefficient of vulcanisation."
J. J. S.

Practical Estimation of Alkyl Groups. HERMAN DECKER (*Ber.*, 1903, 36, 2895—2897).—An apparatus for the estimation of alkoxyl groups by Zeisel's method is described, in which all contact of acetic or hydriodic acids with cork is avoided, and the whole apparatus can be supported by a single stand. The washing-bulbs of the apparatus are charged with 0.5 gram of phosphorus suspended in 25—30 c.c. of water. The water in the jacket is heated in an ordinary wash-bottle, connected with the water supply and the jacket by india-rubber tubing. For substances from which methoxyl is readily removed, the use of acetic acid thus being unnecessary, the apparatus may be simplified by the substitution of a cork-connection with the boiling flask for the sealed-on flask. In some cases observed by Decker and Solonina (*this vol.*, i, 838), the ethoxyl was only completely removed by boiling 3—4 hours with saturated hydriodic acid. On the other hand, *N*-alkyl is sometimes so readily removed as to be mistaken for *O* alkyl, as in the case of 8-nitroquinoline methiodide. In these cases, heating in a



current of carbon dioxide without addition of hydriodic acid will generally remove the alkyl iodide quantitatively. C. H. D.

Some Chemical Constants of Fossil Resins. ROBERT A. WORSTALL (*J. Amer. Chem. Soc.*, 1903, 25, 860—871).—The acid numbers, iodine values, and comparative rates of oxidation have been determined for the following resins: Kauri copal, Manila copal, Pontianac copal, fossil copals of South Africa and West Africa, Sierra Leone copal, Brazilian copal, and Dammar resin. Methods are described for the estimation of the moisture, insoluble matter, ash, insoluble organic matter, indirect acid number, iodine absorption, and colour of resins. E. G.

Dependence of the Temperature Coefficient of the Specific Rotation of Sucrose on the Temperature and Wave-length. OTTO SCHÖNROCK (*Zeit. Ver. deut. Zuckerind.*, 1903, 569, 650—653).—For a normal sucrose solution (containing in 100 true c.c. at 20° C., 26 grams of sucrose weighed in air with brass weights), the temperature coefficient of the rotation less the coefficient of expansion of the length of layer of liquid has the value -0.000469 for sodium light ($\lambda = 589.3 \mu\mu$), -0.000465 for the yellowish-green mercury line ($\lambda = 546.1 \mu\mu$), and -0.000427 for the blue mercury line ($\lambda = 435.9 \mu\mu$); these numbers are practically independent of the temperature. The temperature coefficient of the rotation of the same solution for sodium light has the values -0.000242 at 10°, -0.000184 at 20°, and -0.000121 at 30°.

In practice, if a normal sugar solution is made up at 20°, but polarised at t° in a saccharimeter, the quartz-wedge compensator of which is also at t° , the reading in degrees Ventzke must be increased by $0.061(t - 20)$ in order to obtain the true hundred point of the scale at 20°. T. H. P.

Estimation of Cellulose and Lignin in Foods and Fodders. JOSEF KÖNIG (*Zeit. Nahr.-Genussm.*, 1903, 6, 769—781).—Three grams of the air-dried substance are boiled for 1 hour in a reflux apparatus with 200 c.c. of glycerol of sp. gr. 1.23 containing 2 per cent. of sulphuric acid. After cooling and diluting to 500 c.c., the mixture is boiled once more and the hot solution passed through an asbestos filter. The residue on the filter is washed with 400 c.c. of boiling water, then with alcohol, and finally with a mixture of alcohol and ether until the washings are colourless. The filter and residue are dried at 110°, weighed, ignited, and again weighed. The difference in the weighings corresponds with the amount of "crude fibre" in the substance.

A second quantity of the substance is treated with glycerol and sulphuric acid as above described. The "crude fibre" obtained together with the asbestos filter are placed in a beaker and acted on by 100 c.c. of 3 per cent. hydrogen peroxide and 10 c.c. of 24 per cent. ammonia solution. After 12 hours, 10 c.c. of 30 per cent. hydrogen peroxide are added, and this addition is repeated five times or until the "crude fibre" is completely bleached. Five c.c. of 24 per cent. ammonia are added with the 3rd and 5th quantities of hydrogen peroxide. The

whole is now warmed for 2 hours in a water-bath, and then passed through a second asbestos filter, the operation being completed as before. The weight of cellulose thus obtained is subtracted from the "crude fibre" to give the amount of lignin.

W. P. S.

Solera's Test and New Methods for the Detection of Thiocyanic Acid. DOMENICO GANASSINI (*Chem. Centr.*, 1903, ii, 466—467; from *Boll. Chim. Farm.*, 1903, 42, 417—423).—The author has obtained satisfactory results with Solera's test for thiocyanates. A few drops of the concentrated solution are added to 10 drops of a strong aqueous solution of iodic acid, when free iodine will be formed together with cyanogen iodide.

Several additional tests for thiocyanates are given. (a) The solid substance is moistened with a drop of alcohol containing a trace of cobalt nitrate, which will cause a blue spot. (b) To the solid substance is added a trace of ammonium molybdate, then a drop of hydrochloric acid, and the whole is then exposed to the vapour of hydrogen sulphide, which will cause a violet coloration. (c) The solid or dissolved substance is mixed with a trace of lead peroxide, and then with a drop of acetic acid, when lead sulphate and hydrogen cyanide will be found among the products. (d) The substance, when heated with aqueous potassium hydroxide and then with acids, yields hydrogen sulphide and carbon dioxide. (e) To the solid substance is added 1 or 2 drops of a clear solution of red lead in a 15 per cent. solution of tartaric acid, the mass is evaporated to dryness, and then moistened with strong aqueous potassium hydroxide, which causes a black spot owing to formation of lead sulphide. A characteristic crystalline double compound of potassium thiocyanate with mercuric cyanide also affords a means of detection.

L. DE K.

Ferric Chloride as a Reagent for Tartaric, Oxalic, and Citric Acids. L. ROSENTHALER (*Arch. Pharm.*, 1903, 241, 479—480).—When ferric chloride is added gradually to a solution of a tartrate, an amorphous precipitate is obtained eventually, soluble in alkalis and in mineral acids, but not in acetic acid. With oxalates and acetates, a precipitate is also obtained, but only in dilute solutions.

If a little ferric chloride solution is added to strong solutions of tartaric, oxalic, and citric acids, yellow, pale green, and brownish-yellow colorations are obtained respectively. With strong solutions of the salts, instead of the free acids, the colorations are respectively brown, green, and yellowish-green. These coloured solutions exhibit the reactions of the ferric ion only to a slight degree, presumably because the iron compounds they contain are but little dissociated electrolytically.

C. F. B.

Occurrence and Estimation of Organic Acids in Wine. ALFRED PARTHEIL [and, in part, W. HÜBNER] (*Arch. Pharm.*, 1903, 241, 412—435).—The following solubilities were determined with a view to their use in the separation of the organic acids in wine. A weighed excess of the salt was shaken for 3 days in a bottle im-

mersed in the water of a thermostat, and then either the strength of the solution or the amount of salt undissolved was determined. Water and alcohol of sp. gr. 0·8092 were used as solvents, and determinations were made at 18° and 25°; the numbers quoted are grams dissolved by 100 grams of the solvent:

		Water.		Alcohol.	
		18°.	25°.	18°.	25°.
Lead succinate,	$C_4H_4O_4Pb$	0·0253	0·0285	0·0028	0·0030
Calcium „	$C_4H_4O_4Ca, H_2O$	1·4240	1·4358	0·0014	0·0014
Barium „	$C_4H_4O_4Ba$	0·3961	0·4103	0·0015	0·0016
Silver „	$C_4H_4O_4Ag_2$	0·0176	0·0199	Nil.	
Lead malate,	$C_4H_4O_5Pb, 3H_2O$	0·0288	0·0650	0·0048	0·0048
Calcium „	$C_4H_4O_5Ca, H_2O$	0·9214	0·8552	0·0049	0·0059
Barium „	$C_4H_4O_5Ba$	1·2400	1·3631	0·0038	0·0039
Silver „	$C_4H_4O_5Ag_2$	0·1190	0·1216	Nil.	
Lead tartrate,	$C_4H_4O_6Pb$	0·0100	0·0108	0·0028	0·0032
Calcium „	$C_4H_4O_6Ca, 4H_2O$	0·0185	0·0295	0·0187	0·0235
Barium „	$C_4H_4O_6Ba, H_2O$	0·0256	0·0270	0·0320	0·0356
Silver „	$C_4H_4O_6Ag_2$	0·2012	0·2031	Nil.	
Lead citrate,	$(C_6H_5O_7)_2Pb_3, H_2O$	0·0420	0·0534	0·0156	0·0167
Calcium „	$(C_6H_5O_7)_2Ca_3, 4H_2O$	0·0850	0·0959	0·0065	0·0089
Barium „	$(C_6H_5O_7)_2Ba, 7H_2O$	0·0406	0·0572	0·0044	0·0058
Silver „	$C_6H_5O_7Ag_3$	0·0277	0·0284	Nil.	

Lactic acid volatilises with steam, but slowly; if superheated steam is blown into its aqueous solution, it can be volatilised completely in a comparatively short time. In this way, lactic acid was separated from samples of Rhine and Moselle wines, and identified by the analysis of its barium and zinc salts. The distillate only contains some of the acid in the free state, so as to be measurable by direct titration. The greater part is present in the form of anhydrides, and can be measured by hydrolysing with a known excess of boiling alkali and titrating the excess with a standard acid solution.

When lactic acid or a lactate is heated with concentrated sulphuric acid, carbon monoxide is evolved (Pelouze, *Annalen*, 1870, 53, 221); the reaction is quantitative, so that 1 c.c. of gas, at 0° and 760 mm. pressure, corresponds with 0·004022 gram of lactic acid. A solution containing 0·1226 gram of lactic acid was heated for $\frac{1}{2}$ hour on the water-bath with excess of barium hydroxide, concentrated, rinsed into a small distillation flask, and evaporated to dryness in this under diminished pressure. When the flask was quite cold, the neck was fitted with a stoppered funnel, in which some concentrated sulphuric acid was placed; a few c.c. of the acid were allowed to flow on to the cold, dry residue, and the side tube of the flask was connected with a gas burette. The flask was then warmed cautiously, and the gas evolved washed with potassium hydroxide solution and measured. In three experiments, the volume of carbon monoxide obtained corresponded with 0·1231, 0·1214, 0·1220 gram of lactic acid respectively.

Three samples of wine were examined by this method. The volatile acids were titrated with *N*/10 potassium hydroxide in the manner officially prescribed; excess of alkali was then added, the whole boiled for a

time, and the excess of alkali titrated with acid. The resulting solution was evaporated to dryness and the lactic acid in the residue determined as described above. The results of the three estimations are tabulated below, the numbers representing grams per 100 c.c. of the wine :

Lactic acid	0.041	0.049	0.039
Acetic acid, corrected	0.162	0.097	0.108
" "	uncorrected (from <i>direct</i> titration of the volatile acid, <i>all</i> reckoned as acetic)			0.174	0.108	0.120

C. F. B.

Estimation of Malonic Acid by means of Potassium Permanganate. E. DURAND (*Ann. Chim. anal.*, 1903, 8, 330—332).—Malonic acid or its salts may be titrated with potassium permanganate in a solution containing a little free sulphuric acid and heated to 80°, the end reaction being sharply defined. The products are carbon dioxide, water, and formic acid, which is only oxidised by prolonged contact with permanganate. Three atoms of oxygen absorbed represent one molecule of malonic acid.

L. DE K.

Detection of Boiled and Unboiled Milk. FRANZ UTZ (*Milch.-Zeit.*, 1903, 32, 417—418. Compare this vol., ii, 114).—A reply to Wirthle, who has stated that the reagent used by the author, Ursol D, is identical with *p*-phenylenediamine already recommended by Storch for the differentiation of boiled and unboiled milk. The author, having investigated the matter, arrives at the following conclusions.

(1) *p*-Phenylenediamine and Ursol D iii are identical, but with these Ursol D i and ii are not identical, consequently (2) the author's process is not identical with the method proposed by Storch. (3) The reaction with Ursol D i and ii also takes place in the presence of thiocyanates, which is not the case with *p*-phenylenediamine and Ursol D iii. (4) The author's process is also useful for the detection of hydrogen peroxide in boiled milk.

L. DE K.

Detection of Raw Milk in Heated Milk. FRANZ UTZ (*Milch.-Zeit.*, 1903, 32, 594—595).—A solution of crystallised guaiacol in the presence of hydrogen peroxide gives an orange coloration with raw milk, but no reaction is obtained with heated milk. The solution keeps for a long time and the test will detect 5 per cent. of raw milk in boiled milk. The reaction is not affected by the acidity of the milk or by the presence of ordinary preservatives (compare Abstr., 1902, ii, 539).

W. P. S.

Assay of Beeswax. KARL DIETERICH (*Chem. Zeit.*, 1903, 27, 808); RAGNAR BERG (*ibid.*, 986. Compare this vol., ii, 702).—A controversy on the determination of the iodine number of beeswax.

Berg recommends that the iodine should be allowed to act for some 12 hours before titrating the excess.

L. DE K.

Estimation of Formaldehyde in Solution. G. LEMME (*Chem. Zeit.*, 1903, 27, 896).—Two hundred and fifty grams of crystallised sodium sulphite are dissolved in 750 c.c. of water, a few drops of phenolphthalein are added, and the liquid is carefully neutralised by means of a solution of sodium hydrogen sulphite. To 100 c.c. of this solution are now added exactly 5 c.c. of the formalin to be tested. The formaldehyde at once converts the normal salt into sodium hydrogen sulphite, with which it then combines, whilst a corresponding amount of sodium hydroxide is set free; the latter is then titrated with normal sulphuric acid. One c.c. of acid represents 0.03 gram of formaldehyde.
L. DE K.

Estimation of Cinnamaldehyde. JOSEF HANUŠ (*Zeit. Nahr.-Genussm.*, 1903, 6, 817—827).—About 0.2 gram of cinnamon oil is thoroughly diffused by shaking in 100 c.c. of water. A hot solution of 0.35 gram of semioxamazide in 15 c.c. of water is then added, and the mixture agitated from time to time for 24 hours. The precipitate formed is collected on a filter, washed with cold water, and dried at 105°, a constant weight being obtained in about 5 hours. The weight of precipitate multiplied by 0.6083 gives the amount of cinnamaldehyde in grams.

The aldehyde may be estimated in cinnamon by distilling 8 grams of the latter, finely powdered, in a current of steam. Four hundred c.c. of distillate are collected (which takes about 2 hours). The distillate is extracted several times with ether, the ethereal solution is evaporated at a temperature of 70°, and the residue of oil treated as above mentioned. The author found from 1.96 to 2.04 per cent. of cinnamaldehyde in various samples of cinnamon.
W. P. S.

Estimation of Urea [in Urine] with Mercuric Nitrate. JOHN H. LONG (*Chem. Centr.*, 1903, ii, 313—314; from *J. Amer. Med. Assoc.*, 1903).—A mercuric nitrate solution is prepared of such a strength that 20 c.c. show exactly 0.200 gram of urea in 20 c.c. of liquid. The end reaction is reached when a drop of the liquid gives a decided yellow coloration with soda solution. Twenty-five c.c. of the urine are then mixed with 25 c.c. of baryta solution, and 20 c.c. of the filtrate are neutralised with nitric acid and then titrated. After deducting 2 c.c. as due to uric acid, ammonia, and creatinine, and also allowing for the influence of the chlorides, the amount of urea is read off on a table.
L. DE K.

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 Bilipurpurin.
 Brazilin.
 Butein.
 Carminic acid.
 Catechin.
 Chlorophyll.
 Currenin.
 Daphnetin.
 Galangin.
 Gallein.
 Dimethylindigotins.
 Hæmatoxylin.
 Hæmerythrin.
 Hæmocyanin.
 Hæmoglobin.

Colouring matters. See :—

Hemi-indigotin.
 Hesperitin.
 Indigotin.
 Indirubin.
 Isatin.
 Kampheride.
 Kampherol.
 Lipochrome.
 Mesoporphyrin.
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 - Glucogallin.
 - Gratioligenin.
 - Gratiolin.
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 - Methylglucosides.
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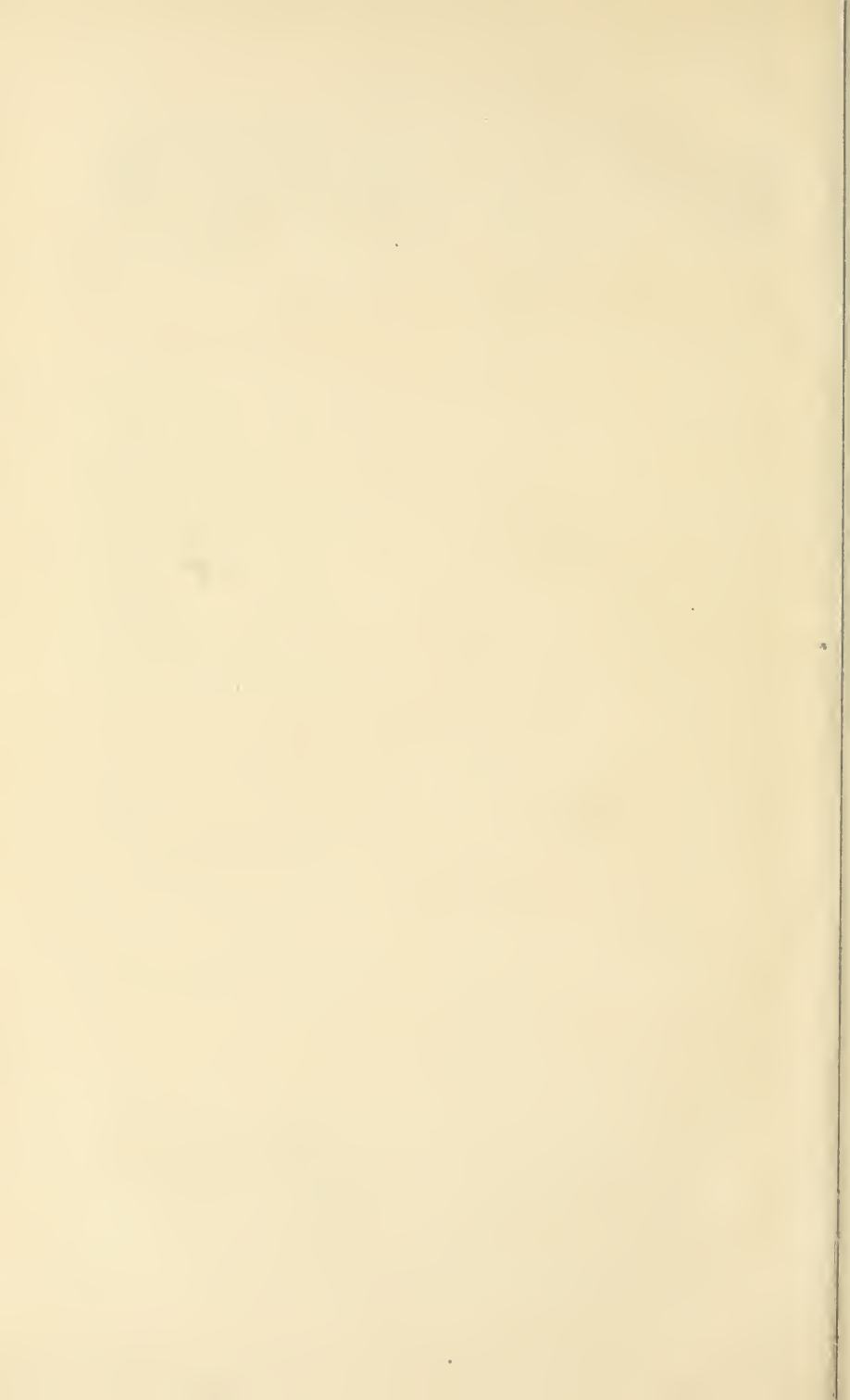
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Zirconium, separation of iron, quantitatively, from (GEISOW and HORKHEIMER), A., ii, 109.

Zoisite, red, from Moravia (SLAVÍK), A., ii, 557.



ERRATA.

VOL. LXX (ABSTR., 1896).

PART II.

Page	Line	
314	7*	for "Weidmann" read "Weidman."

VOL. LXXX (ABSTR., 1901).

PART II.

170	6*	for "Weidmann" read "Weidman."
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VOL. LXXXII (ABSTR., 1902).

PART I.

793	14*	for "jugloe" read "juglone."
793	14*	,, "8-hydroxy-" read "5-hydroxy-."

INDEX.

Page	Col.	Line	
749	i	21*	for "Harlay, Vaughan" read "Harlay, Victor."
,,	,,	16*	,, "Harlay, Vaughan" read "Harley, Vaughan."

VOL. LXXXIV (ABSTR., 1903).

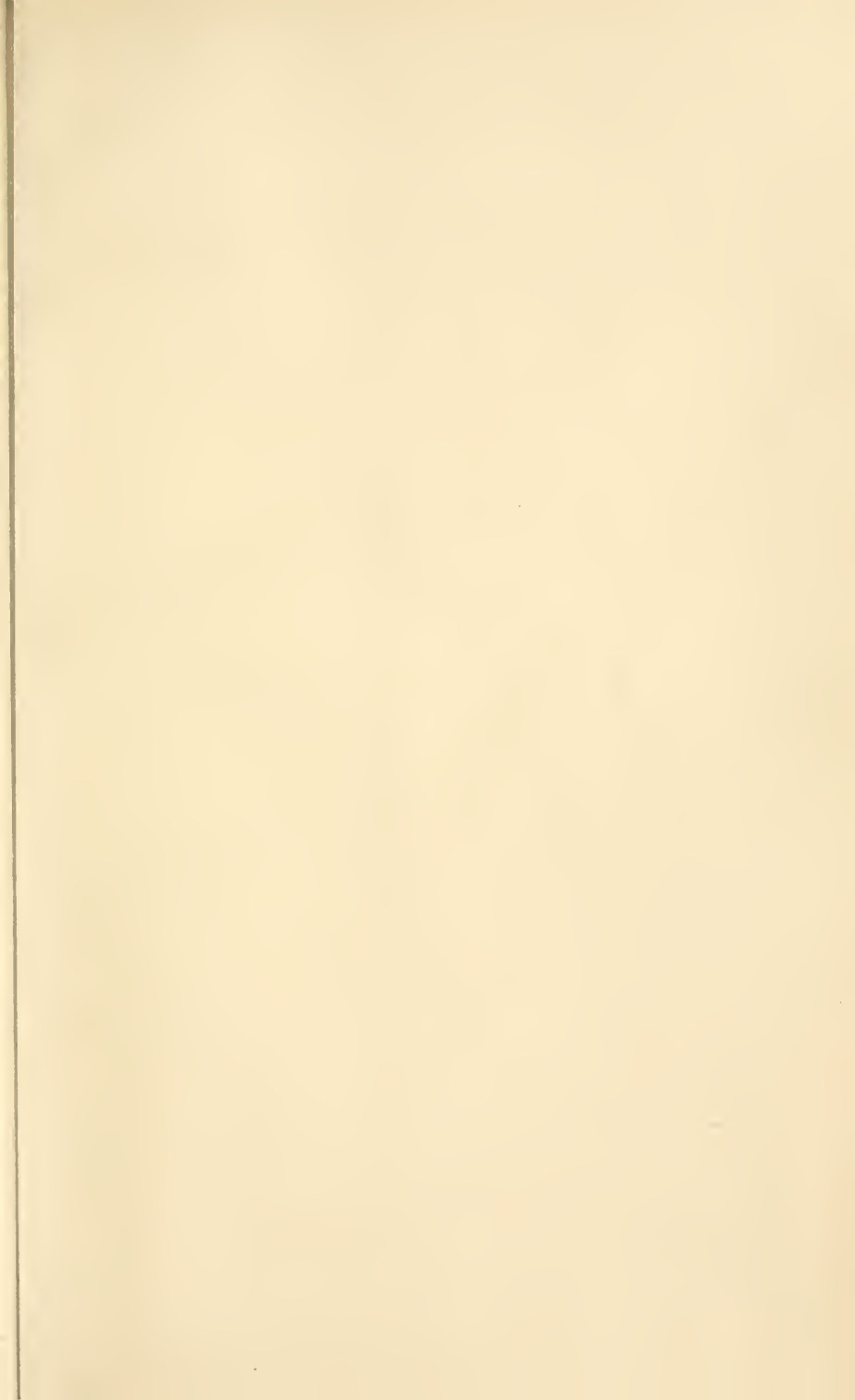
PART I.

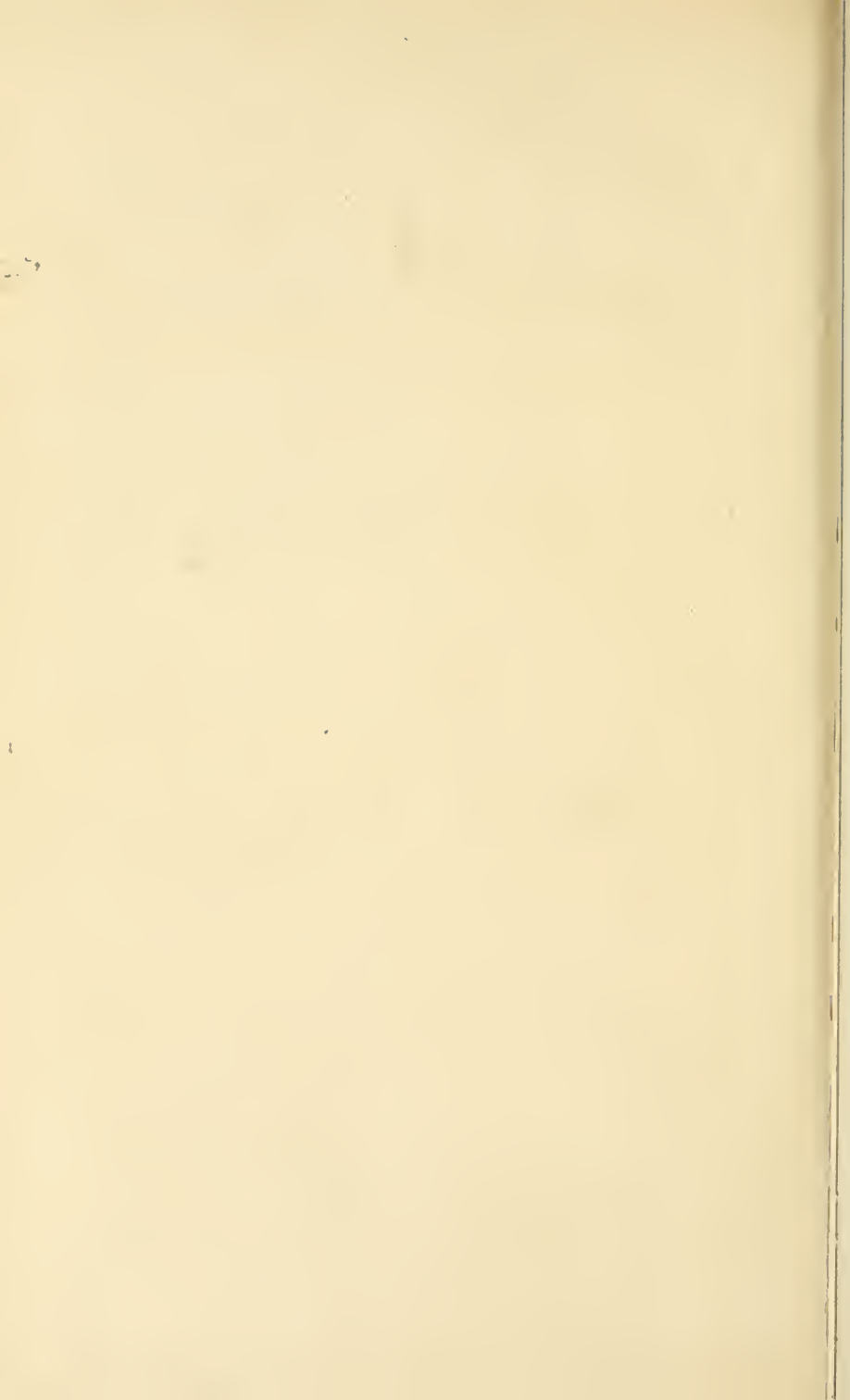
Page	Line	
56	19*	for "its carboxylic acid" read "phenylketoquinazoline-2'-carboxylic acid."
57	5*	,, " $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{N:CMc} \end{smallmatrix} \text{NPh}$ " read " $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{N:CMc} \end{smallmatrix} \text{NH}$."
172	9	,, "benzylideneacetoacetate" read "benzylideneanilineacetoacetate."
185	$\left\{ \begin{array}{l} 19* \\ 17* \\ 11* \end{array} \right\}$,, "Cadinine" read "Cadinene."
398	12	,, "nonylene- α -dicarboxylic acid" read "nonane- α -dicarboxylic acid."
477	10*	,, "a colour" read "an odour."
478	8*	,, "4-Choro-2-nitroanisole" read "4-Chloro-2-nitroanisole."
484	21*	,, "Benzoylcyanate" read "Benzoylcarbimide."
,,	18*	,, "Benzenesulphonyl cyanate" read "Benzenesulphonylcarbimide."
574	16	,, "2-styryl-6-methylpyridine" read "2-p-methylstyryl-6-methylpyridine."
,,	22*	,, "2:6-distyrylpyridine" read "2:6-di-p-methylstyrylpyridine."
631	13-14	,, "Ethyl α -Bromopropionylphenyl Acetate" read "Ethyl α -Bromopropionylphenylacetato."
663	3*	,, "Az.N ₃ " read "Ar.N ₃ ."
684	11*	,, "zinc oxide" read "zincoxide."

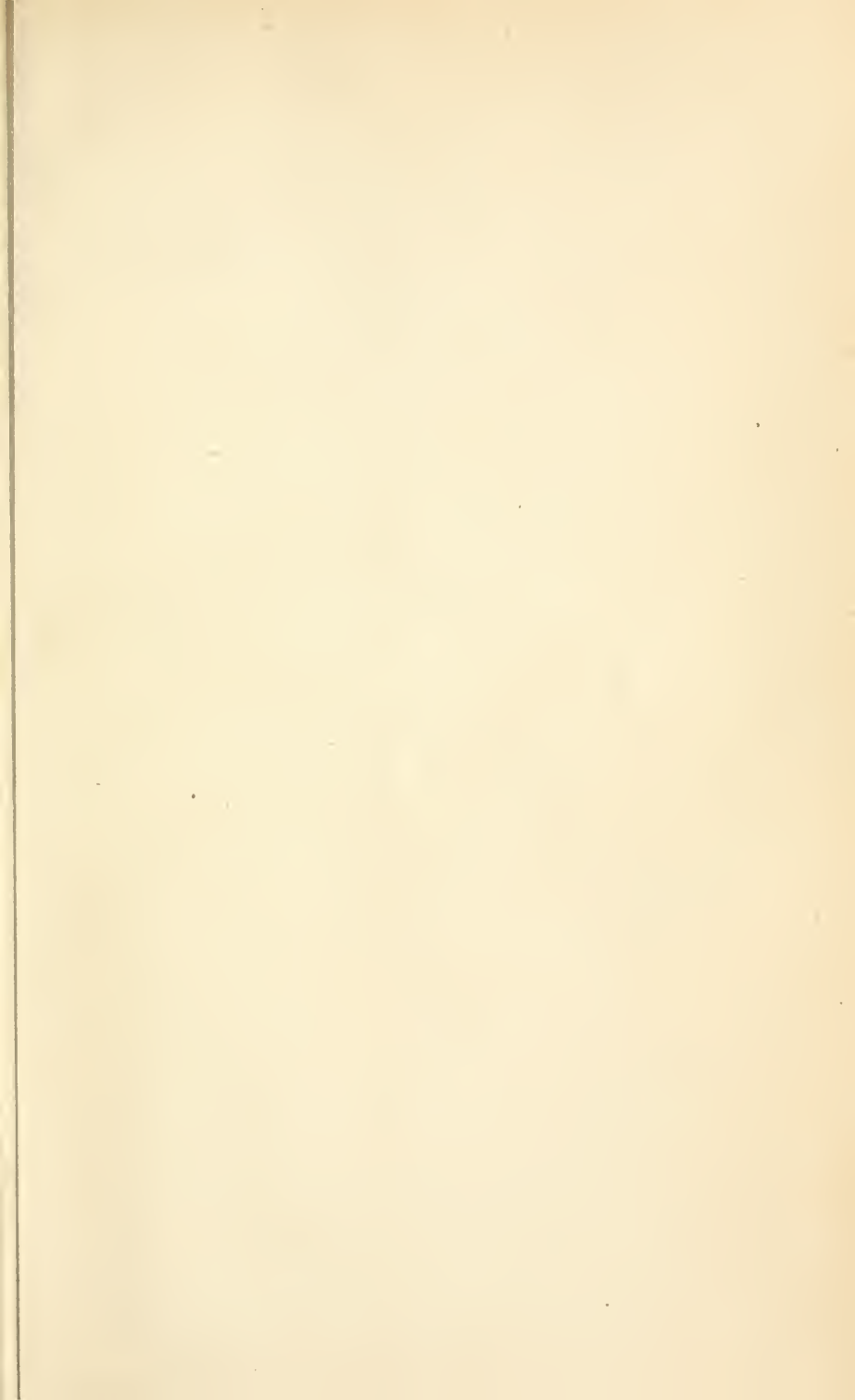
PART II.

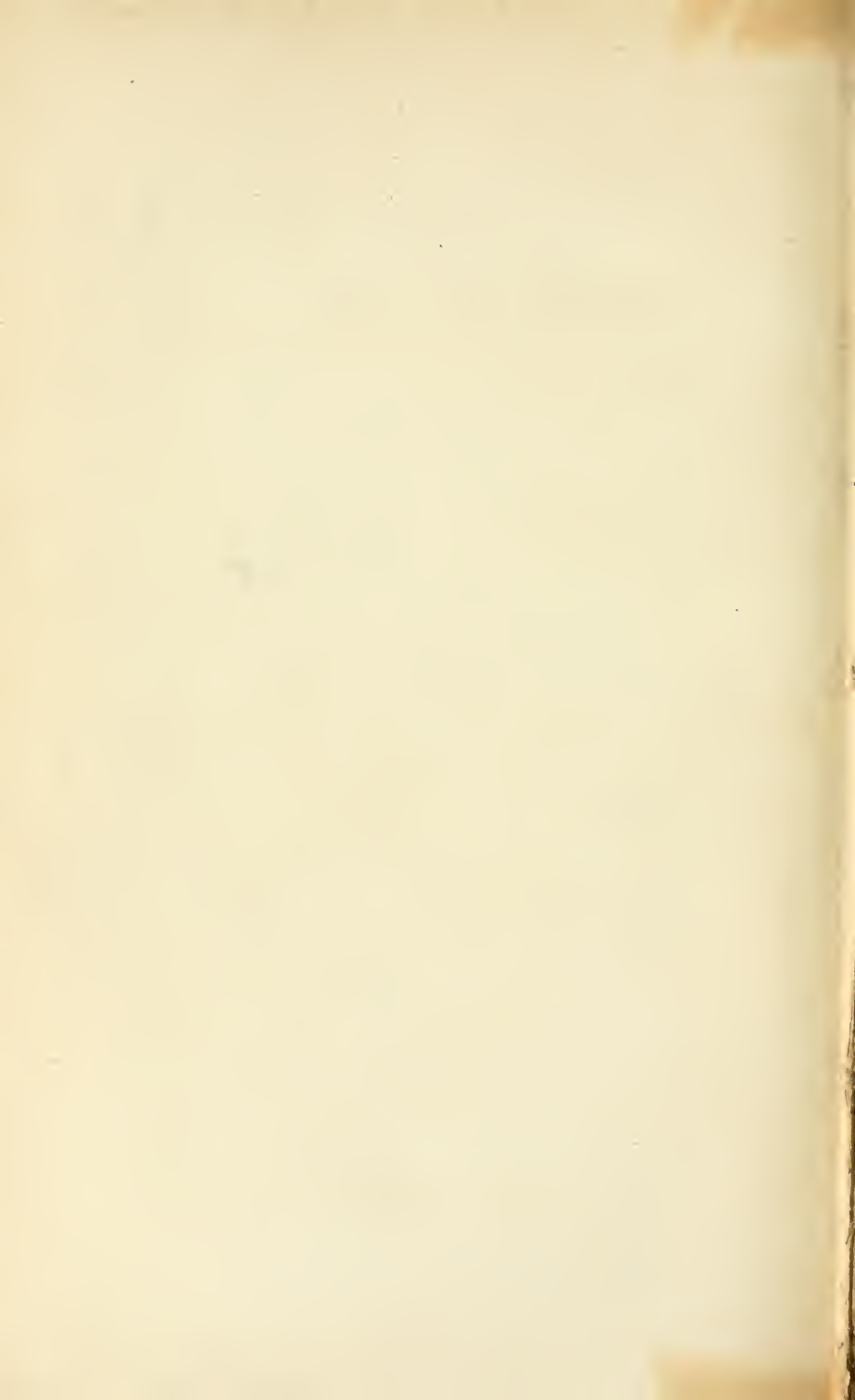
Page	Line	
29	30	<i>for</i> "chlorastolite" <i>read</i> "chlorastrolite."
148	3*, 2*	,, "When a solution of dimereuriammonium nitrite is stirred into concentrated nitric acid by means of a pipette," <i>read</i> "When strong nitric acid is dropped from a pipette on to dimereuriammonium nitrite,"
223	17*	Huelvite is from Huelva in the south of Spain, not from the Pyrenees.
334	13	<i>for</i> "copper" <i>read</i> "zinc."
335	9	,, "arsenic or antimony" <i>read</i> "or arsenic or antimony when fully oxidised as described."
410	12*	,, "Barium ammonium" <i>read</i> "Bariumamide."
444	20	,, "ALAY" <i>read</i> "ALOY."
492	2	,, " <i>Jahresb</i> " <i>read</i> " <i>Jahresh.</i> "
534	8*	,, "1/4th—1/8th" <i>read</i> "1·4th—1·8th."
534	6*	,, "1/3rd—1/6th" <i>read</i> "1·3rd—1·6th."
549	10	,, "GEUSSLER" <i>read</i> "GENSSLER."
594	23	,, "preceding" <i>read</i> "following."

* From bottom.









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